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$$\int \frac{dx}{x(ax+b} = \frac{1}{b} \ln \frac{\quad}{ax+b.}$$

DIFFERENTIAL EQUATIONS
IN
APPLIED CHEMISTRY

BY

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PREFACE

This book is based on a course given in recent years to students in Chemical Engineering at the Massachusetts Institute of Technology. It is similar in grade of difficulty to the "Differential Equations" of Dr. H. B. Phillips, from which it differs in containing more Chemistry and less Mechanics.

It would be impossible to mention all the sources from which the problems have been taken. A large number of them are due to Professor W. K. Lewis, who was the first to recognize the need of such a course and who has given the authors many valuable suggestions. Some of the simpler problems on rate of reaction have been adapted from "Chemical Statics and Dynamics" by J. W. Mellor, a work to be commended as collateral reading. The method of treatment, however, has for the most part evolved in the actual course of class-room teaching, and is believed to be largely new.

The purpose of the book is not to teach Chemistry, but to teach Mathematics in a form readily assimilated by Chemists and Chemical Engineers. And just as Chemistry itself cannot be well understood except as a branch of Science in a wider aspect, so the principles of Mathematical Chemistry are often most clearly brought out by the study of problems much broader in their application than any specific technical requirement. The practical needs of the Chemical Engineer are, however, constantly kept in sight. Much emphasis is placed on graphic methods and on numerical work. After careful consideration the answers to the problems have with few exceptions been omitted. The authors believe that a chemist or an engineer, or a young

man about to become an engineer, should possess sufficient stability of mind to check his own calculations.

A few of the more difficult problems lead to differential equations of a type whose solutions have never been worked out. These may be of interest to the advanced reader in suggesting topics for research.

The authors will be grateful to anyone pointing out misprints or other errors.

FRANK L. HITCHCOCK
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DIFFERENTIAL EQUATIONS IN APPLIED CHEMISTRY

CHAPTER I

INTRODUCTION

1. Why Chemists require Mathematics. — Mathematics may be defined as "that science which treats of numbers and magnitude, or of whatever is capable of being numbered or measured."* Its business is to examine the facts within its scope, — that is, all processes or quantities which can be numbered or measured, — and so to classify and analyse them that they may be used with advantage and with decreased labor. Such a definition is very broad. If we accept it as true it follows that we shall include physics, chemistry, and engineering within the realm of mathematics.

These branches are indeed often called the mathematical sciences in contradistinction both to the fine arts and to those sciences which are purely descriptive or historical. It is a very significant fact, however, that at the present day all phases of human thinking tend to become more analytical and more exact, for such is the very spirit of a scientific age. If there are exceptions, they occur precisely where we should expect them, namely in some developments of the fine arts; but such subjects as economics, biology, geology, and even anthropology, where formerly a rigorous quantitative treatment was almost unknown, are being brought more and more within the viewpoint, and to some

* Worcester's *Comprehensive Dictionary.*

degree within the actual working methods of the mathematician.

It may then be taken as the function of mathematics to assist in the classification and analysis of the facts regarding physics, chemistry, and the like; and its success in growing from an abstract science into a broader field of usefulness is measured by what can be accomplished by its aid.

2. Calculus as a Tool. — Mathematics in the rather vague language of common use is often divided into "lower" and "higher." There is no sharp line of division. Calculus is more fundamental than Analytical Geometry or Trigonometry. It is not only a method of exact thinking but includes labor-saving devices and short cuts for obtaining results. It may possibly be true that, as has sometimes been said, there is no result obtainable with calculus which could not (conceivably) be obtained without it. But the labor involved would frequently be prohibitive, and the methods would be so complex that no human mind could find them out.

The need for labor-saving methods of thought in chemistry and chemical engineering is greater now than ever before. The calculus is a labor-saving tool of the greatest importance. The chemist or engineer who fails to make use of it in the solution of problems is handicapping himself. In these days of strong competition and of the elevation of the fittest he who masters its use will find himself amply repaid.

The first object of this book is to help students in chemistry and chemical engineering to think more readily in terms of calculus. Most engineering schools give excellent courses in differential and integral calculus, usually during the first two years of the four years' course. This is necessary in order to enable the student to handle readily the fundamental subjects of physics, physical chemistry, applied mechanics, and so forth. However, when the more specialized work of the fourth year is reached he is better ready to

appreciate the bearing of differential equations upon the material in hand. It is not our purpose to review in any systematic way his previous mathematical studies, although references to them will be frequent and occasionally detailed. Still less is it intended to teach him in this little book the technical problems of his profession with any completeness, even though the examples given him to work are selected with direct reference to actual chemical practice. Some of them are based on investigations carried on at the Massachusetts Institute of Technology in recent months. The purpose is rather to lead him into fresh fields of thought, where he may find a broader point of view, and whence he may at the same time regain a stronger hold of the fundamentals and learn to apply them to his professional work, discovering the value to himself of this wonderful tool. Perfect mastery in technical problems comes only with long practice. This book may serve to acquaint him at least with the existence of the tool.

3. The Scope of this Book. — The point of view of the authors may be indicated by an allegory. Suppose a geologist and an artist to be taking a stroll together through a varied landscape. Each sees the same hills and valleys, but to one observer his habits of thought tend to present these scenes to his mind as so many scientific questions, while to the other they are more likely to be material for his brush and easel. The purpose of this book will be attained in so far as the student acquires the habit of seeing the phenomena of life and of nature, including his professional work, as so many examples which might be set up in the language of differential equations.

Accordingly the reader will find in the following pages various problems which may seem at first remote from chemistry, — questions on the growth of populations, on colonies of bacteria, on the age of the earth, and on the rate of drying of a wet sheet hung in the wind. As his familiarity

with the new mode of thought increases, however, he will come to see all these as cases of " mass action", words which have a familiar sound to every chemist. He will be able to say more exactly just what he means by the mass law, and he will note that the logic by which, from a study of radioactive changes in rocks, their age is estimated, is very similar to that by which he can learn to stop a chemical process at precisely the moment to obtain the best yield. Or from the simple matter of the wet sheet, he will work toward the complex types of drying apparatus used by the chemical engineer. And he will note that laws of growth and decay, whether they govern the rise and fall of a race of men, or of an empire, or of a culture of bacteria, are plotted by curves of a form very similar to those governing standard types of chemical processes. The fact that cultures of bacteria are themselves of great use in some chemical operations is interesting and important, yet of minor significance in learning the method of thought. The increase in population in early New England times is a still better, because very simple, illustration of the mass law, — in spite of the fact that the Puritans possessed few chemical industries.

The two-fold object which most of the problems in this book possess, of providing concrete illustrations of fundamental principles while at the same time working toward the actual necessities of chemical engineering, is to be specially noted in connection with the series of problems on the flow of fluids. This series runs through the whole book. It begins in Chapter I with the problem of washing brine out of a tank. There does not seem at first much to be gained by wasting the good salt in this way. But in the first place these problems on flow offer the best mechanical model of " consecutive processes," — witness the use made of them in that fascinating book " The Interpretation of Radium " by F. W. Soddy. And in the second place they introduce the student directly to chemical processes of

the continuous current type which are commercially important.

To sum up what has been said thus far, the first object of the student should be to *learn the language of calculus*, so that he may *express all these problems in the form of differential equations* with the same ease with which he might express himself in any other language which he has mastered. And as with any other language, mastery requires much practice.

Furthermore the student has two other important needs in the way of mathematical technique. These are

1°. How to integrate the differential equation.

2°. How to perform the calculations needed to obtain an answer correct within the practical requirements of the problem.

4. The Fundamental Concept of Calculus. — In chemical processes, and indeed in all processes involving changes, the first step is frequently to *study the rate at which changes take place, and to analyse the causes of these changes.* In the ordinary language of mathematics the expression "rate of change" is used for indicating the rapidity of change of one variable quantity as compared with another variable quantity. In discussing the rate of an engineering process we have to consider not only the quantity whose change we especially desire to analyse called the *dependent variable*, but also the *independent variable*, or quantity with which the dependent variable is compared.

It is also important to distinguish clearly the two concepts "*rate of change*" and "*average rate of change.*" For example, in chemical reactions the *average* velocity with which the reaction takes place is measured by dividing the quantity changed during a specified interval of time by that time. The *rate of change at any instant* is the *derivative of the quantity with respect to the time*, and is expressed as

$\frac{dx}{d\theta}$, where dx represents the amount of the change of the quantity x during the time $d\theta$.

While the expression " rate of change " is usually applied to changes involving *time as the independent variable*, there are a great many types of changes which do not explicitly do so, but which resemble time changes in character and behaviour. It is convenient to speak of the rate of these changes also, the independent variable being necessarily specified in every case, and it will be found that the method of analysis used for studying time changes will apply equally well to the others.*

5. Integrating the Differential Equation. — The task of integrating the differential equation which occurs in a chemical problem may be simple or difficult, according to the nature of the problem. It is a happy circumstance that many of the most common and important problems are very easy in this respect, yielding differential equations of the " separable " type, or at worst are " linear " and therefore are already familiar to the student in proportion to his thoroughness in the calculus of the second year. A few harder cases will occur from time to time.

A large proportion of these elementary types integrate in terms of natural logarithms. It would seem that Nature, on her physical and chemical side, has a peculiar fondness for the quantity e, the base of the natural system of logarithms, a fact which the mathematician may justify by remarking that e^x is its own derivative. The student has usually had little or no practice in manipulating logarithmic expressions and solving equations in which they occur. Such practice will inevitably be supplied in abundance if he works out the problems in the following chapters. The properties of logarithms as laid down in some good text-

* For a fuller discussion of rates of change and of derivatives, consult Woods and Bailey's Elementary Calculus, Chapters I and II, or other standard textbook on calculus.

book on trigonometry or algebra may well be reviewed, but the explanations of the present text have been made very detailed and will probably be sufficient.

6. Numerical Calculations. — In regard to the important matter of numerical calculation, there are three available methods in most problems, first, the use of tables including the slide rule, second, reduction of the problem to one in progression, and third, the use of graph paper. Usually a happy combination of all these is best. As they are all taken up in detail in their proper place no further introductory remarks are necessary, except to emphasize that, to the engineer as to the mathematician, the test of workmanship is in the soundness of his arithmetic. There is a real test of character in the answers a man will turn in. This test does not reside alone in their accuracy and freedom from blunders, essential qualities though these of course are. We may illustrate by citing two common cases of answers which we regard as vicious. One student has a question for which he is expected to return an answer correct to three significant figures, the right answer being 75.4; he knows what is required of him and sets out with every fair and good intention to get it, but by, it may be, hasty work with a slide rule, he gets 73.2 and will then complain bitterly because he is given only a little credit for the problem. Many a promising engineering job has failed to function for similar cause, but the excuse of this man usually is that " chemical engineers don't need to know the answer better than five per cent."

A second man, — or more likely the same man next time, — has a question where the experimental data by no stretch of interpretation can be correct to better than two significant figures. By zealous work with pencil or tables an answer such as 3.075398 is produced. Probably this result is more immoral than the former, since it has an appearance of accuracy which does not exist.

The honest method of handling figures is simple and easily stated:

1°. Decide how many significant figures it is desirable to find.

2°. Decide whether the data warrant this or a smaller number.

3°. Make it a matter of religion to get exactly the number you have decided upon.

7. Summary. — The object of this introductory chapter has been to point out the value of calculus as a tool for the chemist, and to emphasize that mastery of it requires exercise of the mental faculties in no immature way; first in analysing the problem and translating it into mathematical language, second in integrating or otherwise solving the resulting differential equation, and third in calculating the answer in a form suitable for practical use. The qualities of mind and the manipulative skill required for the three operations are quite distinct but all of value to the engineer. They are to be kept in view in all the work of this book.

CHAPTER II

PROCESSES OF THE FIRST ORDER

8. Definition of a First Order Process. — In many chemical reactions it is found that the rate of change of one substance into another is proportional to the first power of the concentration of the first substance. In these cases the velocity of the reaction at a given time depends only on the amount of the reacting substance at that time, provided the other conditions of the reaction — such as temperature, etc. — remain constant. A reaction of this type is known to chemists as a *reaction of the first order*. And in other types of changes than chemical reactions it is frequently found that the rate of change of one variable as compared with another variable is proportional to the first power of the one variable alone. Such a change will therefore be spoken of as a *process of the first order*.

To express a process of the first order in mathematical form, suppose that in a certain process involving the material x, the rate of change of x is proportional to the amount of x present. This would be a process of the first order. The rate of change of x (with respect to time) is $\frac{dx}{d\theta}$, as pointed out in Chapter I. The process can therefore be expressed mathematically by the differential equation

$$\frac{dx}{d\theta} = kx \qquad (1)$$

where k is a " constant of proportionality " to be determined by some suitable means.

The present chapter deals with processes of the first order. As a step toward a scientific understanding of natural proces-

ses it is of the greatest importance to consider the question: why do so many of the commoner and simpler phenomena obey (at least approximately) an equation of the form (1)? The illustrative examples which follow below will suggest various answers to this question. Broadly speaking it may be said that equation (1) is a mathematical statement of the simplest case of that very general principle roughly known as the " Law of Mass Action."

As an illustration, it appears to be true in the breaking down of radium atoms into smaller atoms, that for example out of one trillion radium atoms, the number which will explode per day is quite definite and fixed, independently of all external conditions whatever. It is evident that, if this be so, ten trillion atoms will yield ten times as many exploded particles per day as one trillion, or that, in general, the decay of radium follows the law (1). This also indicates that the percentage decomposed per day is a constant, independent of the amount present, a fact that will be shown to apply mathematically, for all first order processes.

Or again, take the case of a culture of bacteria with abundant food supply and no toxic conditions. If all other circumstances remain constant any group of a thousand bacteria will tend, by their natural law of growth, to increase in numbers just as fast as any other group of one thousand. The total rate of growth will, therefore, be proportional to the total number of bacteria present, in agreement with an equation of the form (1).

Similarly, it is known in the theory of sound that the amount by which an organ pipe must be shortened to produce a rise of a semi-tone in pitch is proportional to the length of the pipe, other things being equal. This is why, in a pipe organ, the tops of every set of pipes seem to lie on a curve of definite character. When equation (1) has been integrated and the character of the integral studied in detail, it will appear that the graphical representation of

a first order process of any kind is a curve which may be called " logarithmic " or " exponential " according to which of the variables we consider as independent.

Example (*A*). It is known that the rate of inversion of cane sugar in dilute solution is proportional to the concentration of the unaltered sugar. (This was the result of experiment, of course.) If the concentration was 1/100 when $\theta = 0$ and was 1/250 when $\theta = 5$ hours, express the concentration as a function of the time θ.

Solution. Let the concentration of the unaltered sugar at time θ be called c. Then

$$\frac{dc}{d\theta} = kc \tag{2}$$

which is to be integrated under the assumption that the time is reckoned from the start of the experiment, that is, $c = c_0$ when $\theta = 0$. By " separation of variables " (multiplying by $d\theta$ and dividing by c), the differential equation may be written:

$$\frac{dc}{c} = k\,d\theta \tag{3}$$

One way to solve this differential equation is to integrate both sides in the form

$$\ln c = k\theta + \text{const.} \tag{4}$$

where " const." denotes the constant of integration, and where $\ln c$ is the " natural logarithm " of c, that is, the logarithm to the base 2.71828 + denoted by e. (One reason why this base is properly called the *natural* base is that it enters inevitably and naturally in so many problems of physics and chemistry.) To determine the constant of integration we have the fact that $c = c_0$ when $\theta = 0$, which gives by substituting in (4)

$$\ln c_0 = \text{const.} \tag{5}$$

and by inserting this value of the constant in (4) we find

$$\ln c = k\theta + \ln c_0 \tag{6}$$

or, since the difference of the logarithms of two quantities is the same as the logarithm of their quotient, the equation may be written in the form

$$\ln \frac{c}{c_0} = k\theta \tag{7}$$

(Equation (7) may also be obtained from (3) by taking the *definite* integral of both sides of (3) between proper limits, thus

$$\int_{c_0}^{c} \frac{dc}{c} = \int_{0}^{\theta} k\, d\theta \tag{8}$$

which gives (7) directly.)

Now equation (7) holds true for all corresponding pairs of values of c and θ. Suppose that at a time θ_1 it was observed that $c = c_1$. Then

$$\ln \frac{c_1}{c_0} = k\theta_1 \tag{9}$$

Dividing (7) by (9) so as to eliminate k, and partially clearing of fractions gives

$$\ln \frac{c}{c_0} = \frac{\theta}{\theta_1} \ln \frac{c_1}{c_0} = \ln \left(\frac{c_1}{c_0}\right)^{\frac{\theta}{\theta_1}} \tag{10}$$

where the last step follows because the logarithm, to any base, of a quantity raised to some power is the same as the index of the power times the logarithm of the quantity, an elementary and frequently used property of logarithms. Finally, since the logarithms of two expressions can be equal only when these expressions themselves are equal,

$$c = c_0 \left(\frac{c_1}{c_0}\right)^{\frac{\theta}{\theta_1}} \tag{11}$$

which is the desired relation between the concentration c and the time θ. Inserting the given data $c_0 = 0.01$, $c_1 = 1/250$, $\theta_1 = 5$,

$$c = 0.01\ (0.4)^{\frac{\theta}{5}} \tag{12}$$

Remarks on the above solution. The equation (11) is a relation connecting the values of c at three different times. It may therefore be called the " three-point formula " for a first order process.

The right member of (11) may be written in several other forms which are useful. For instance let

$$r = \left(\frac{c_1}{c_0}\right)^{\frac{1}{\theta_1}} = \text{a constant} \tag{13}$$

equation (11) then becomes

$$c = c_0\, r^{\theta} \tag{14}$$

showing the analogy between a first order process and a geometric progression.

It is to be noticed that, in working out the numerical solution of the above example, a literal solution was first obtained, the data afterwards substituted. This order of work is to be preferred when practicable for two reasons, first it yields a general result useful in all similar problems, and second it is usually quicker and more accurate.

Example (*B*). Van t'Hoff found that 5.11 grams of dibromsuccinic acid decomposed in hot water at the following rate:

When θ =	0	10	20	30	40	50	60	minutes
Acid =	5.11	3.77	2.74	2.02	1.48	1.08	0.80	grams

Set up an equation of the form (2) and calculate k for each of the times given. Is k sufficiently constant to indicate a reaction of the first order?

Solution. Letting c stand for the number of grams acid remaining at time θ, integrating as in Ex. (A), and solving equation (7) for k,

$$k = (\ln c - \ln c_0) \div \theta \tag{15}$$

from which k may be calculated by a table of natural logarithms. To use common logarithms advantage is taken of the relation

$$\ln c = 2.303 \log c \tag{16}$$

where log denotes the logarithm to base 10. Thus

$$k = (\log c - \log c_0)\,(2.303) \div \theta \tag{17}$$

Using four-place logarithms and arranging the calculation in tabular form we find:

$$\log c_0 = \log 5.11 = 0.7084$$

θ	$\log c$	$-\log (c/c_0)$	$-\ln(c/c_0)$	$-k$
10	0.5763	0.1321	0.3041	0.03041
20	0.4378	0.2707	0.6232	0.03116
30	0.3054	0.4031	0.9281	0.03094
40				
50				
60				

The calculations for the last three observations are left to the student.

Example (*C*). A tank contains 100 gallons of brine, the amount of dissolved salt being 50 pounds. Fresh water is allowed to run into the tank at the rate of three gallons per minute, the brine overflowing at the same rate. The solution is kept practically uniform by agitation. How much salt will there be in the tank at the end of one hour?

Solution. The simplest way to set up a differential equation for problems on rate of flow is to state the obvious relation

$$\text{increase} = \text{inflow minus output} \tag{18}$$

Considering an interval of time $d\theta$ the relation (18) may be stated more at length thus: the increase dc which takes place in the amount of salt in the tank during time $d\theta$ is the difference between the amount of salt flowing in during this time and the amount flowing out. This fact is axiomatic provided no chemical reaction or other cause creates or destroys salt inside the tank. It is equally evident that

$$\text{inflow} = (\text{rate of flow of solution})\,(\text{concentration})\,(\text{time}) \tag{19}$$

with a similar relation for output, and also

$$\text{concentration} = \text{total salt} \div \text{volume} \tag{20}$$

Calling V the volume of brine, c the total salt at time θ, it is clear that in this problem the inflow of salt is zero since the incoming liquid is fresh. The concentration of the outgoing solution is c/V and the rate of outflow of solution is 3 gal./min. Hence

$$\text{output of salt} = 3\frac{c}{V}d\theta \tag{21}$$

meaning that in an interval of time $d\theta$ short enough so that during this interval the concentration does not sensibly change the number of pounds of salt which leaves the tank is $3\,c\,d\theta/V$ or $0.03\,c\,d\theta$ since the volume of brine is constant at 100 gals. Substituting in (18)

$$dc = -0.03\,c\,d\theta \tag{22}$$

Integrating in the form (7) gives

$$\ln\frac{c}{50} = -0.03\,\theta \tag{23}$$

To solve this equation for c, use the important property of logarithms

$$e^{\ln q} = q \tag{24}$$

where q is any quantity whatever. (This is merely one form of the definition of a logarithm.) Therefore from (23)

$$c = 50\, e^{-0.03\theta} \tag{25}$$

Putting $\theta = 60$ min. and using a table of exponentials gives $c = 8.265$ lbs. (Another good way is to write (23) in the form

$$2.3\,(\log c - \log 50) = -0.03\,(60) \tag{26}$$

then solve for $\log c$ and use a table of common logarithms.)

Example (*D*). The air in a recently used class-room $30 \times 30 \times 12'$ tested 0.12% by volume of carbon dioxide. How many cubic feet of fresh air must be admitted per minute in order that ten minutes later it shall contain not over 0.06%? (Fresh air contains 0.04% CO_2.) Assume immediate mixing of fresh with stale air.

Solution. Set up equation (18). Adopt the notation

y = concentration of CO_2 by vol. at time θ
a = cu. ft./min. of entering air.
V = vol. of room.
y_0 = concentration CO_2 at start.
g = concentration CO_2 in fresh air.

It is then evident by (19) that, in time $d\theta$,

$$\text{inflow} = ag\,d\theta \tag{27}$$

and, since stale air leaves by leakage through doors and windows at the same rate at which fresh air enters,

$$\text{output} = ay\,d\theta \tag{28}$$

The total CO_2 at time θ is Vy, by a relation like (20). Hence the increase in time $d\theta$ is $d\,(Vy)$ or $V\,dy$, since V is constant. Filling in equation (18)

$$V\,dy = ag\,d\theta - ay\,d\theta \tag{29}$$

The easiest way to solve this differential equation, and at the same time to see that the process is of the first order, is to introduce a new variable x defined by

$$x = y - g \tag{30}$$

whence $dx = dy$ because g is a constant and drops out on differentiation and (29) may be written

$$\frac{dx}{d\theta} = -\frac{a}{V}x \tag{31}$$

which is of the form (1) and shows the value of k to be $-\frac{a}{V}$, that is

$$a = -kV \tag{32}$$

making it clear that the unknown a is found when we find k. Proceeding as in Example (A), equation (8),

$$\int_{x_0}^{x} dx/x = k\int_{0}^{\theta} d\theta \tag{33}$$

and solving for k as in (15)

$$k = (\ln x/x_0) \div \theta \tag{34}$$

or by (32)

$$a = -V(\ln x/x_0) \div \theta \tag{35}$$

which by (30) is the same as

$$a = -\frac{V}{\theta}\ln\frac{y-g}{y_0-g} \tag{36}$$

We now insert the data of this example, $V = 10{,}800$, $\theta = 10$, $y = 0.0006$, $y_0 = 0.0012$, $g = 0.0004$ and have

$$a = -\frac{10{,}800}{10}\ln\frac{0.0006-0.0004}{0.0012-0.0004} = -1080\ln 1/4$$

$$= +1080\ln 4 = 1080\,(1.386) = 1500 \text{ cu. ft. approx.}$$

Remarks on the above solution. The process here employed of introducing an auxiliary variable to reduce the differential equation to the form (1) is very important. Its significance will appear more fully on considering the two important properties of first order processes next to be given:

1°. The geometrical progression property.
2°. The semi-logarithmic property.

9. The Geometrical Progression Property. It has already appeared in equation (14) that a formal resemblance exists between a first order process and a geometric progression. This becomes a real resemblance when the exponent θ is an integer. For any term of a geometric progression is equal to the first term multiplied by an integral power of the ratio r. The analogy may be more fully stated thus:

If a quantity varies according to a differential equation of the form (1), and if in some definite interval of time the quantity is known to change by a certain fraction of its value, it will change by the same fraction during any other equal interval of time.

This fact is most frequently used by stating the time in which a variable, obeying equation (1), falls to half its value. For instance the rate of decay of the radioactive substance thorium X is such that the activity falls to half its value in four days. Or the length of an organ pipe is halved for every octave of rise in pitch, other things being equal. But there is no special virtue in the fraction one-half except simplicity, and the principle is of great use in calculation.

Example (E). Using the result of Example (C), find how much salt remains in the tank after two hours.

Solution. Instead of putting $\theta = 120$ and solving (25) or (26) we note that the salt fell to $\frac{83}{500}$ of its value in one hour.

Therefore in two hours its value will be

$$50\left(\frac{83}{500}\right)^2$$

which is readily computed by a slide rule.

Example (F). With everything as in Example (D), find what would be the concentration of CO_2 if the same current of fresh air could be continued for a second period of ten minutes.

Solution. It is important to notice first that it is the variable x and not y which satisfies the equation of form (1). Now x at the start was $y_0 - g$ that is 0.0012 − 0.0004 or 0.0008. After ten minutes x has fallen to 0.0006 − 0.0004 or 0.0002. Thus x has fallen to $\frac{1}{4}$ its value in 10 min. By the G. P. property x will in another ten minutes fall to $\frac{1}{4}$ of its value 0.0002 or 0.00005, and y will become 0.00045 or 0.045 %.

Remark on the last two solutions. In practice it often happens that problems on first order processes can be solved mentally or with slight labor using the G. P. property, which would be otherwise lengthy. This will usually be true when the time intervals which occur are multiples of some common divisor.

10. The Semi-logarithmic Property. — One of the most convenient ways of studying a process is to devise some method of plotting on graph paper so that the graph shall be (approximately) a straight line. If the process is of the first order there are two excellent methods of doing this.

First Method. By inspection of equation (17) it appears that if we plot log c as ordinate against θ as abscissa on ordinary graph paper, the result will be a straight line, providing always that c and θ are connected by the differential equation (1). The data of Example (B) may therefore be easily tested to see if the process is of the first order by making such a plot, without actually calculating the constant k.

The points obtained will lie on a straight line, due allowance made for experimental error and for possible actual departure of the phenomena from a true first order process. The verification is left to the student. When making the plot, the following suggestions should be borne in mind: —

1. Choose a piece of graph paper $6'' \times 6''$ or larger, ruled decimally — whether in centimeters or inches is a question of taste.

2. Make a table of the values to be plotted. In the data of Example (B), the first column θ is abscissa against the second column log c as ordinate.

3. Make a horizontal and a vertical scale such that the largest and the smallest values to be plotted fall near the respective ends of the scale. The full extent of the scale will thus be utilized.

4. In marking points, estimate tenths of a scale division by the eye, and neglect values smaller than a tenth. Points are best indicated by small finely drawn + signs.

Second Method. It is often convenient to plot the same graph by using semi-log paper. We plot c as ordinate against θ as abscissa, using for c the scale already printed on the graph, with suitable introduction of the decimal point. Paper may be obtained with either one, two, three or four log scales to the page. The graph is continued across the page as many times as necessary, each journey across the page being numbered, and a corresponding scale indicated on the margin. It is evident that these successive passages over the page will indicate a set of parallel lines. It is thus possible to graph on a single page a wide range of the variables more conveniently than with ordinary paper, though sometimes with less accuracy.

The method of plotting on semi-log paper is illustrated in Fig. 1, which is a graph of Example (A), carried from $\theta = 0$ to $\theta = 18$ hours. During this time the concentration

of the unaltered sugar falls from 0.01 to 0.00037. The horizontal scale is divided into six equal intervals, each corresponding to one hour, so that three journeys across the page in

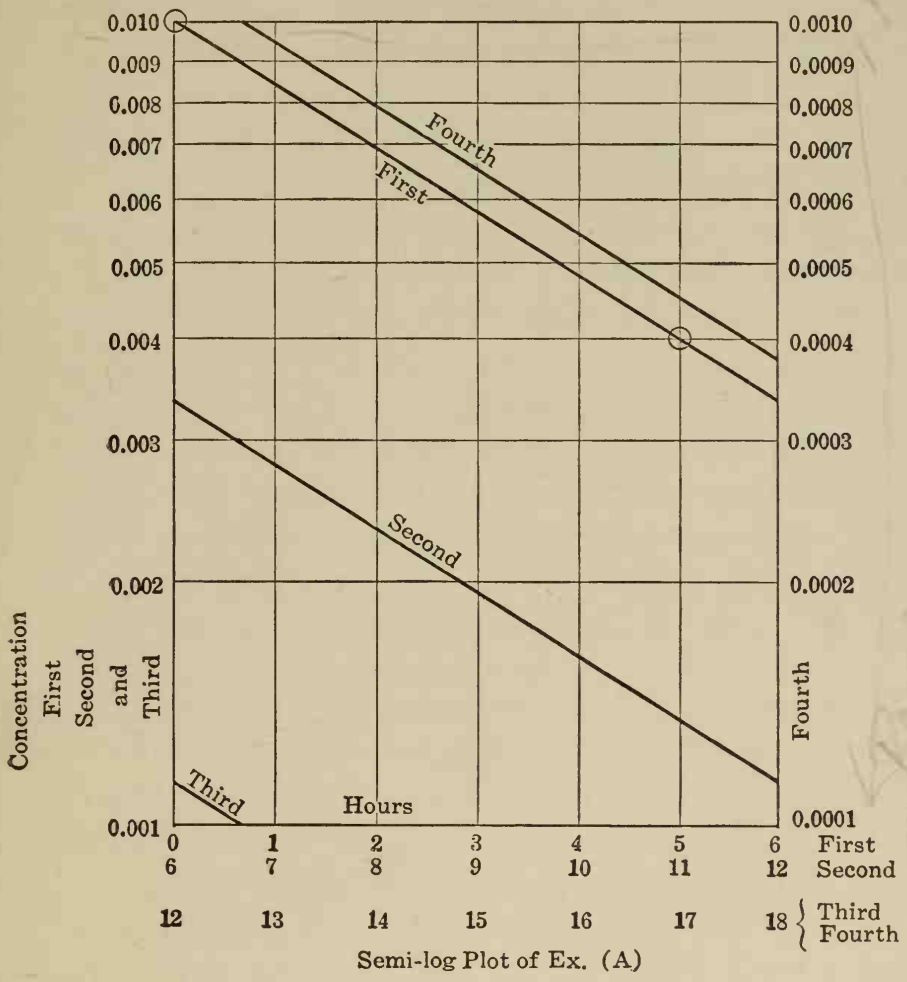


FIG. 1.

the horizontal direction are required to cover eighteen hours. The vertical scale is logarithmic. On the left of the diagram the decimal point has been so placed that we may begin at the top with the concentration 0.01, corresponding to $\theta = 0$, and end at the bottom with the concentration 0.001, corresponding to approximately $\theta = 12.6$. On the right of the diagram the decimal point has been moved one place to the left, giving 0.001 at the top and 0.0001 at the bottom.

The graph consists of four straight lines numbered in order. The first covers the time from 0 to 6 hours, the second from 6 to 12 hours, while the third and fourth, which together make one horizontal journey across the figure, cover the time from 12 to 18 hours. On the other hand, the first, second, and third pieces of the graph together make one journey from top to bottom, and cover the change in concentration from 0.01 to 0.001. The fourth piece is part of a second journey in the vertical direction, beginning at 0.001 and ending at 0.00037. The plot was made by first noting the two observations given in the text, namely $c = 0.01$ when $\theta = 0$, and $c = 0.004$ when $\theta = 5$. These are indicated by two small circles about the points in question. A straight line is drawn through these two points and continued with constant direction as described above.

It should be carefully noticed that in extrapolating, that is predicting the course of a process over an interval of time extending far beyond the range of the observed values, three sources of error exist:

1°. Errors in drawing (or calculating). These are likely to be magnified by extrapolation.

2°. A slight error in the slope of the straight line, due to unavoidable experimental errors in the data themselves, may produce a relatively large error in the predicted values.

3°. The actual process almost invariably departs more or less from the assumed law. Such departure may be gradual and progressive, or may be very sudden, according to the nature of the phenomenon.

PROBLEMS

1. With the data of Ex. (A), find the value of c after 13 hours. (Slide rule accuracy is sufficient.)

2. Show that the answer to Ex. (A) may be written

$$c = 0.01\, e^{-0.183\theta}$$

When would this form of answer be convenient? Verify the answer to Prob. 1 by use of this formula.

3. Make the table for $\theta = 40, 50, 60$, in Ex. (B), using four-place logs as in the text. When four-place logs are used, to how many significant figures will the calculations be accurate?

4. Find the average of the six values of k in Ex. (B). What is the greatest per cent departure from this mean value? What is your conclusion in regard to the phenomena? Can any rule be given to govern your decision as to whether the process is of the first order? Is this average value of k the "most probable value?"

5. With the data of Ex. (A), let z denote the amount of invert sugar at time θ. Express z as a function of θ.

6. In a first order reaction does the value of k depend upon the amount of substance present at the start? Does it depend on the unit of mass employed? Does it depend on the unit of time employed?

7. With the notation of Prob. 5, suppose we were able to observe c_0, z_1, z_2, θ_1 and θ_2. Express k in terms of these quantities.

8. With everything as in Ex. (C), after how many hours will the solution contain less than half of one per cent salt by weight? (Slide rule accuracy.)

9. A student working Ex. (C) made the mistake of using equation (11), taking $\theta_1 = 1$, and $c_1 = 48.5$. If his calculation were otherwise correct, what was the per cent error in his answer? (Use four place logs.) Can you state why his logic was bad?

10. Blanksma, when transforming 49.30 gms. acetochloranilid into para-chloracetanilid, observed that 13.70 gms. of the para compound were formed during the first hour, and 9.85 gms. during the second hour. What evidence do these data give that the process is of the first order? (Use G. P. property.)

11. With the data of Ex. 10, how much acetochloranilid would we expect to find unchanged after 8 hours? (Use the G. P. property.) He found actually 4.8 gms. How do you explain the discrepancy?

12. Make a graph of Prob. 10 by plotting the log of the acetochloranilid against the time on ordinary cross-section paper. Read from your graph the number of hours needed for the acetochloranilid to fall to 0.1 gm. How accurately can the time be read? How well does the value of the acetochloranilid read from the graph when $\theta = 8$ agree with the calculated value from Prob. 11? Compare your reading for 0.1 gm. with the rest of the class.

13. Make a graph of Prob. 10 by plotting acetochloranilid against time on semi-log paper. How well can you read the answer to Prob. 11? Read also the time needed for the acetochloranilid to fall to 0.1 gm.

14. Using the data of Ex. (B), plot log c against θ as described in the text. Draw a straight line which shall pass approximately through the seven points, and continue it far enough to read the value of log c when $\theta = 100$. Repeat using semi-log paper.

The following problems are to be solved by first setting up a differential equation which, in each case, may be thrown into the form (1) or (2). The solution may then be completed by using one of the integrated forms, like (7), (11), (17), or (25), or by using the G. P. principle, or by making a graph. The student should not limit himself to a single method, but should select in each case what appears the most convenient. It is well to check the answer by using two different methods. Slide rule accuracy will be sufficient. Ordinary data such as specific gravities may be found from a handbook when needed.

15. If the activity A of a radioactive deposit is proportional to its rate of diminution, and is found to decrease to $\frac{1}{2}$ its value in 3 hours, what is its value after 9 hours? After 13 hours?

16. According to Newton's law, the rate at which a substance cools in air is proportional to the difference between the temperature of the substance and that of the air. If the temperature of the air is kept at 20° C., and the substance cools from 100° to 60° in 20 minutes, when will its temperature become 30°? When 21°?

17. A porous material dries in the open air at a rate approximately proportional to its moisture content. (Can you see a reason why this should be so?) If a sheet hung in the wind loses half its free moisture the first hour, when will it have lost 99 per cent, weather conditions remaining the same?

18. If in the culture of yeast the amount of active ferment doubles in 3 hours, how much may be expected at the end of 15 hours at the same rate of growth? At the end of 20 hours?

19. Hydrogen flows through one tube into a litre flask filled with air and escapes through another. If the current is so slow that the mixture may be considered uniform, what percentage of hydrogen will the flask contain after 3 litres of gas have passed through? How much after 10 litres?

20. Repeat Prob. 19 using oxygen in place of hydrogen. Assume that air contains 21 per cent of oxygen.

21. If the average person takes 18 breaths per min., exhaling each time 100 cu. in. containing 4% carbon dioxide, find the per cent CO_2 in the air of a class room $\frac{1}{2}$ hour after a class of 50 enters. Suppose the air fresh at the start, and the ventilators admit 100 cu. ft. fresh air per min. (Fresh air contains 0.04% CO_2 by volume.) Take volume of room = 10,000 cu. ft.

22. A factory room $200 \times 45 \times 12'$ receives through the ventilators 10,000 cu. ft. fresh air per min., which contains 0.04% of CO_2 by vol. The help enters at 7:00 A.M. A half hour later the CO_2 content has risen to 0.12%. What value is to be anticipated at noon? How much fresh air must be admitted per min. to insure that the CO_2 shall never rise above 0.10%?

In such a problem will the ventilation be better or worse if the fresh air and the foul air do not mix rapidly? If we assume no mixing at all, what will be the differential equation?

23. A lot of leather is washed free from salt which it contains, by suspending it in water in a drum, into which fresh water is flowing at the rate of two gallons per minute. The leather is very thoroughly agitated by rotating the drum and the solution of salt thus formed runs to waste through an overflow pipe as fast as fresh water is admitted. The leather is so thin and porous that the diffusion of the salt into the surrounding solution may be considered as instantaneous in comparison with the rate at which the water is being changed.

The drum contains 500 gals. of water. Each charge contains 400 lbs. of leather on a dry basis; this when taken from the drum and sent to the dry loft contains 600 lbs. of solution in its pores. If at the start of the operation each charge contains 100 lbs. of salt, while the dry product must not exceed 0.4% how long must the washing be continued?

24. The population of New England increased from 26,000 in 1640 to 1,000,000 in 1790, during which interval there was very little immigration. Allowing 30 years to a generation, estimate the average number of children per family, no allowance being made for infant mortality nor unmarried persons.

25. The population of the country is now 100 millions. The natural growth of population would cause the number of inhabitants to double in fifty years if there were no immigration, which, however, brings a constant influx of one million per year. Assuming the natural increase among the immigrant population to be no higher than among the native element, in how many years will the population double?

26. If a quantity increases according to a first order process, what

must be the value of k in order that the rate of growth may be equivalent to 6% interest compounded at the end of every time-unit?

27. Prove that continuous compound interest at 5% is very nearly equivalent to yearly compound interest at 5.1%.

28. If a man can earn 5 dollars a day over expenses, and keep his savings continuously invested at 6% compound interest, how long will it take him to save \$25,000?

29. Consider a vertical column of air, and assume that the pressure at any level is due to the weight of air above. Show that $p = p_0 e^{-kh}$ gives the pressure at any height h, if Boyle's law be used. Determine k from the known properties of air, assuming the temperature of the whole atmosphere to be 0° C.

30. A first order process gave a yield of one gm. during the first hour and 0.7 gm. during the second hour. What was the total yield?

31. In every gram of radium, 15×10^{10} atoms change per sec. into the emanation. Find how long for $\frac{1}{2}$ the radium to be changed. Given that 1 c.c. of hydrogen contains 2.7×10^{19} molecules, and the atomic weight of radium is 226.

Ans. about 1900 years.

32. The element thorium, which is not itself radioactive, changes into active thorium X at a substantially constant rate. The active thorium X may be separated from its parent thorium by precipitation with ammonium hydroxide, the active part remaining in the filtrate. After the filtration it is found on the one hand that the activity of the filtrate falls to $\frac{1}{2}$ its value in 4 days, and, on the other hand the precipitate recovers activity on standing. Find how long before the precipitate will recover $\frac{1}{6}$ the former activity.

33. With the data of Prob. 32, what fraction of its original activity will the inactive thorium recover in 1 hour? In 5 days?

34. Some radium chloride in solution, of normal activity 1000, was deprived of its emanation by a rapid current of air. It was then allowed to stand air-tight for 105 mins., when its activity was found to be 13.1. Find the radioactive constant k for the decay of the emanation.

CHAPTER III

PROCESSES OF THE SECOND ORDER

11. Definition of Second Order Processes. In the usual language of chemists, a reaction is said to be of the second order when the rate of the reaction is proportional to the product of the concentrations of two reacting substances, or, as a special case, to the square of the concentration of one reacting substance. To say the same thing in mathematical symbols, let c and c' be the concentrations of the two reacting substances, and x the concentration of one of the products. If the reaction proceeds in agreement with the differential equation

$$\frac{dx}{d\theta} = kcc' \tag{37}$$

it is said to be of the second order.

If a and b denote the amounts of the two substances present at the start, and if our unit of measure is the gram-equivalent of each substance, it follows that

$$c = a - x, \qquad \text{and} \qquad c' = b - x \tag{38}$$

by which (37) takes the form

$$\frac{dx}{d\theta} = k\,(a - x)\,(b - x) \tag{39}$$

This differential equation may be described in mathematical language by saying that the derivative of the dependent variable with respect to the independent variable is equal to a polynomial of the second degree in the dependent variable.

Many processes other than chemical reactions proceed in agreement with a differential equation like (39). By analogy with the language of the chemist, these will be called processes of the second order.

Remark. It must not be said, however, that the differential equation itself is of the second order, for to the mathematician this would mean the presence of the second derivative $\frac{d^2y}{d\theta^2}$. That a word shall be used in different senses by different people and at different times appears a law of nature difficult to alter, a fact, at least, which is true of the word *order* even within the domain of mathematics. No confusion is caused, because a mathematician is exceedingly careful about his language. In this book, intended not so much for mathematicians as for chemists who wish to absorb mathematical ideas, it appears better to employ a term in a way familiar already. The two expressions " process of the second order " and " differential equation of the second order " will cause no confusion, particularly since there will be little occasion for use of the latter, more mathematical, term.

Differential equations like (39) occur very frequently in that type of chemical reaction known as metathesis.

Example (*G*). Reicher found that 0.5638 gram mols of sodium hydroxide acted on 0.3114 gram mols of ethyl acetate at the following rate:

When θ	=	0	393	669	1010	1265
alkali	=	0.5638	0.4866	0.4467	0.4113	0.3879
ester	=	0.3114	0.2342	0.1943	0.1589	0.1354

Show that the reaction is of the second order.

Solution. The chemical equation is as follows:

$$NaOH + C_2H_5Ac = C_2H_5OH + NaAc$$

On the assumption that the reaction is substantially non-reversible, the rate of formation of the alcohol would be

proportional to both the concentration of the hydroxide and that of the ester. If a and b denote respectively gm. mols of alkali and of ester at the start, and x the mols of alcohol at time θ, then $a - x$ and $b - x$ will be the mols alkali and ester left to react at time θ. Hence x will satisfy (39) provided this conception of the nature of the reaction is true.

To try it out, proceed as in Example (B). Integrate (39) between appropriate limits,

$$\int_0^{x_1} \frac{dx}{(a - x)(b - x)} = \int_0^{\theta_1} k \, d\theta \qquad (40)$$

yielding the result

$$2.3026\left[\log (a - x) - \log (b - x) - \log \frac{a}{b}\right] = (a - b)\, k\theta \quad (41)$$

By making a table after the style of Example (B) it will be seen if k is constant within the limit of experimental error. The trial is left to the student. Four-place tables should be used.

Example (*H*). In a laboratory experiment, spent iron oxide from a gas works, containing 52% of sulphur, was extracted with boiling benzol. The following data were obtained:

Weight of spent oxide = 25 gms.
Weight of benzol = 100 gms.

Time in minutes	0	10	20	30	40	50	60	70	80	90
Concentration	0	2.15	3.4	4.32	5.10	5.73	6.32	6.78	7.04	7.42

where the concentration is expressed as grams of sulphur dissolved per 100 grams of benzol.

The solubility of sulphur in benzol at the boiling point is 11.7 grams per 100 grams of benzol.

It was desired to fit an equation to the data which should represent the facts within the precision of the experiment, about 5 per cent.

Solution. It was first assumed that the rate of solution of the sulphur was proportional to the amount of sulphur left undissolved, which would imply a process of the first order. To test this, the logarithm of the number of gms. of undissolved sulphur was plotted against time. It was found that the best graph through the points was a curve, and not a straight line as it would have been had the process been of the first order.

It was then assumed that the rate of solution of the sulphur was proportional both to the amount of undissolved sulphur and also to the difference between the concentration of the solution and that of a saturated solution at the same temperature. This is actually a more reasonable supposition than the former one, because no sulphur would dissolve when the solution became saturated, even though there remained some undissolved. If the improved conception of the process is true it will be of the second order and the differential equation will be

$$\frac{dw}{d\theta} = -kw\,(S - c) \tag{42}$$

where w is the number of grams of undissolved sulphur at time θ, while S and c are the grams of sulphur per 100 grams boiling benzol in a saturated solution and in the actual solution at time θ, respectively.

This differential equation contains three variables, w, c, θ. But w and c are connected in virtue of the fact that

$$\text{Total sulphur present} = c + w = 25 \times 0.52 = 13 \text{ grams} \tag{43}$$

Hence $w = 13 - c$ and $dw = -dc$ giving

$$\frac{dc}{d\theta} = +k\,(13 - c)\,(11.7 - c) \tag{44}$$

an equation of the form (39). By integrating as in (41)

$$2.3026\left[\log (13 - c) - \log (11.7 - c) - \log \frac{13}{11.7}\right] = (13 - 11.7)\, k\theta \qquad (45)$$

If this equation is a good representation of the process, a plot of the quantity $\log [(13 - c)/(11.7 - c)]$ against θ, using the observed data, should yield a series of points nearly on a straight line.

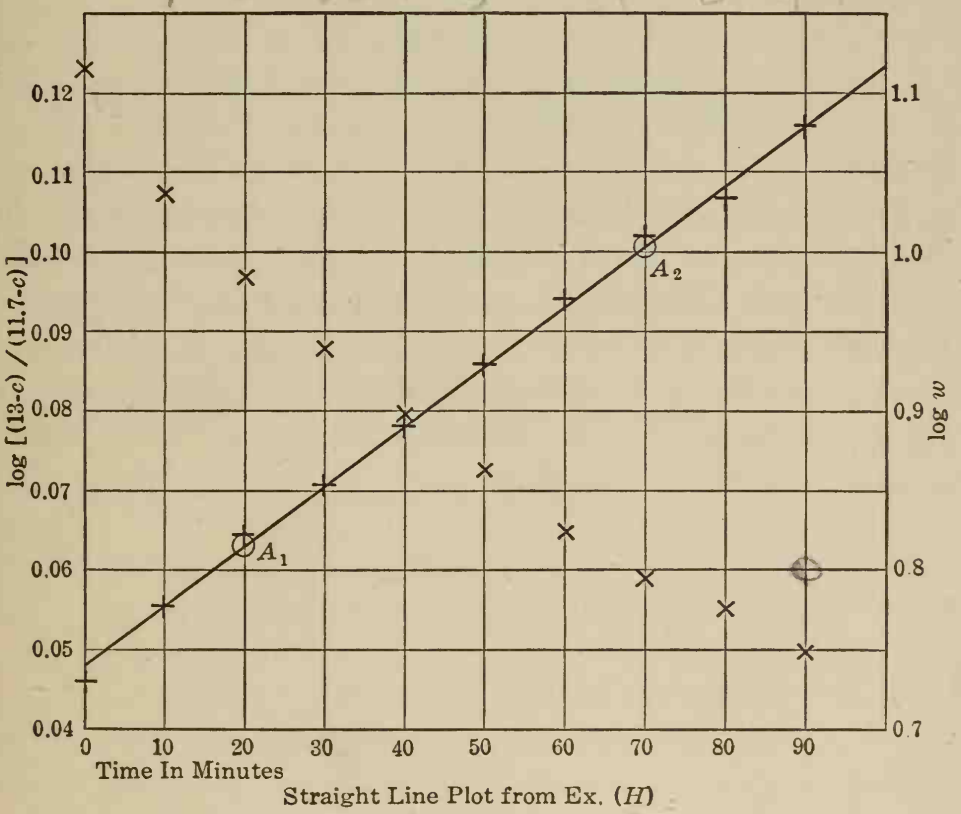


FIG. 2.

Remarks on the above solution. It is interesting to note (Fig. 2), that what appears to be the best straight line through the points does not pass through the point $\left(0, \log \frac{a}{b}\right)$, a fact probably due to a considerable error in observing

the start of the experiment. The actual start seems to differ by about three minutes from that indicated by the first observation.

The two assumptions made as to the rate of solution of the sulphur appear very reasonable when we try to understand the mechanism of diffusion. On the surface of the undissolved sulphur is a thin film of saturated solution. The forces which carry this film off into the neighboring dilute solution are analogous to a difference of potential. That the rate of solution should also be proportional to the amount undissolved is equally natural, for when the soluble material is contained in a mass of inert substance the surface exposed is substantially proportional to the amount present.

12. Finding the Best Line through a Set of Points. — In Example (H) it was seen that the plot of log w against θ gave on the whole a curve and not a straight line. The plot is shown on Fig. 2, where the scale on the right of the page corresponds to log w and the observed points are indicated by the mark $\times$.

The scale on the left of Fig. 2 corresponds to $\log \frac{13 - c}{11.7 - c}$ and the observations are indicated by the mark $+$. These points lie on a straight line, within the limits of experimental error.

This procedure of devising some method of plotting by which a series of points are made to lie nearly on a straight line is very useful, and is the method usually employed in fitting an equation to a set of data. It now becomes important to draw the best straight line through these points. A rough method is merely to draw the line with a ruler, estimating the position by the eye so as to leave about as many of the observed points on one side of the line as on the other.

A slightly more accurate method, and the one used in

plotting Fig. 2, is called the *Method of Averages.* It is shown in works on the *Theory of Probability* and *Method* of *Least Squares* that the most probable straight line through a set of points (under certain assumptions as to the nature of the experimental errors) passes through the point whose abscissa is the average of the abscissas of all the points of the set, and whose ordinate is the average of all the ordinates. That is, to find this *Average Point,* we add together the abscissas (in Example (H) these will be the values of θ) and divide their sum by the total number of points in the group. Similarly we add the ordinates, (in Example (H) these will be the values of $\log\frac{13-c}{11.7-c}$), and divide the sum by the total number of points in the group. The point whose abscissa and ordinate are the numbers thus found will be called the *Average Point of the Group.*

Since two points are needed to determine a straight line, the whole observed set of points is divided into two groups, and the average point of each group is found. In Example (H) are ten observations. The first five and the last five, respectively, were taken, and the average points found. These two points are indicated at A_1 and A_2, Fig. 2, by small circles about the points. Finally the straight line was drawn through these two points by a ruler.

The method of averages is usually quite as rigorous as the data warrant. The equation of the straight line through the two average points may be calculated by analytical geometry, (Woods and Bailey, *Elementary Calculus, Art.* 14). Hence the value of the constant k and the corrected reading for the time at the start of the experiment may be found with greater accuracy than would be possible from only two observations. For fuller discussion, works on the method of least squares may be consulted. For other graphic methods, and many examples, see Lipka's *Graphical and Mechanical Computation,* Chap. VI.

PROBLEMS

1. Make a table for Ex. (G) after the manner of Ex. (B). Hence find the average value of k for Reicher's experiment.

2. In a second experiment Reicher began with 0.3910 gm. mols alkali and 0.6593 gm. mols ester, and found after 342 minutes 0.2885 of alkali and 0.5568 of ester. Calculate the value of k.

3. In Prob. 2 name two conditions essential to the experiment if k is to be the same in both runs.

4. Derive equation (41) from (40). (Lipka's table of integrals may be used.)

5. Solve equation (41) for x. Hence find the amounts of sodium hydroxide and of ethyl acetate to be expected when $\theta = 684$ in the second experiment of Reicher (Prob. 2).

6. Make a graph for the data of Prob. (2) by plotting $\log \frac{a-x}{b-x}$ against θ on ordinary cross section paper. Hence verify the result of Prob. 5.

7. Make a graph for the data of Prob. (2) by plotting $\frac{a-x}{b-x}$ against θ on semi-log paper. Hence verify the result of Prob. (5).

8. Arrange equation (41) so as to show an analogy with geometric progression. State in words the G. P. property of a process of the second order. Use this principle to verify the result of Prob. 5.

9. Use your graph of Prob. 6 to determine the value of k, and compare the result with Prob. 2.

10. Suppose Reicher had used equivalent mols of sodium hydroxide and ethyl acetate, for instance 0.500 mols of each to start, other conditions remaining as before, how long would have been required for half the ester to be decomposed?

11. In the special case of a second order process where $a = b$, how may the data be plotted so as to give a straight line? Using both the data and the result of Prob. 10, make such a plot, and read off the value of the time when the ester shall have fallen to $\frac{1}{4}$ its original value.

12. State in words the property possessed by the special case treated in Probs. 10 and 11 which enabled you to plot a straight line. Hence verify the result of Prob. 11 by a simple calculation.

13. Compare the course of a chemical reaction of the second order with one of the first by plotting the amount of product against time. Use the same axes for both reactions, and assume initial amount of

reacting substances in each case to be one gram mol. and each reaction to be half completed in one hour.

14. If data are available showing the yield of a process for a number of values of the time, and if the initial amount of all the reacting substances is known to be one gram mol., what do you regard as the easiest way to determine whether the reaction is of the first order, or of the second order, or neither? Test the following:

(a) When θ = 0	1.0	1.7	2.5	5.0	10.0	$\propto$	hours
x = 0	0.20	0.29	0.40	0.50	0.70	1.00	mols
(b) When θ = 0	1.0	1.4	3.3	5.0	10.0	$\propto$	hours
x = 0	0.20	0.22	0.25	0.33	0.68	1.00	mols
(c) When θ = 0	5	8	12	20	$\propto$	hours	
x = 0	0.50	0.68	0.82	0.95	1.00	mols	

15. Make a graph of Ex. (G) in the style of Fig. 2. Calculate the value of k by the method of averages. To how many decimal places is it well to compute k? Compare your answer with the result of Prob. 1.

16. A process is known to satisfy a differential equation of the form (39). The value of the constant b is known to be 9.82 mols. The constant a cannot be directly measured. The following observations of x were made:

When θ = 0	20	40	$\propto$	hours
x = 0	5	7.76	9.82	mols.

Find the constants a and k.

17. A mass of inert material containing 5 lbs. of salt in its pores is agitated with 10 gals. of water. In 5 minutes 2 lbs. of salt have dissolved. When will the salt be 99% dissolved?

18. A mass of insoluble material contains 30 lbs. of salt in its pores. The mass is agitated with 20 gals. of water for one hour, when $\frac{1}{2}$ the salt is found to be dissolved. How much would have dissolved in the same time if we had used double the amount of water? (Assume the mechanism of solution to be like the extraction of sulphur in Ex. (H). A saturated solution of salt holds 3 lbs. per gal.)

19. A porous material dries in a confined space as if the moisture it contains were dissolved out by the air. A quantity of material containing 10 pounds of moisture was placed in a closed storeroom of volume 2000 cubic feet. The air at the beginning had a humidity of 25%, (that is, $\frac{1}{4}$ saturation). At the temperature of the storeroom saturated air holds 0.2 lb. moisture per lb. of dry air. If the material lost half

its moisture the first day, estimate its condition at the end of the second day.

(A cubic yard of air weighs approximately two pounds.)

20. How long would be needed for the substance of the preceding problem to lose 90% of its moisture if the humidity of the air is kept at 25% by ventilation?

CHAPTER IV

SIMULTANEOUS PROCESSES

13. Side by Side Reactions. — There are many processes both in chemistry and in engineering which may be most simply investigated by regarding them as the result of two or more simpler processes going on simultaneously. The point of view will be made clear by taking up a number of special cases.

Side Reactions

The expression "side reactions" is an abbreviation for the longer expression "side by side reactions."

Example (*I*). A certain radioactive substance yields two quite distinct emanations, each at a different rate. It is known that the rate of formation of each emanation is proportional to the amount of the parent substance present. Each emanation is formed directly from the parent. Thus the process consists of two simple first order reactions going on side by side.

Call c = amount of substance present at time θ.
x = amount of first emanation at time θ.
y = amount of second emanation at time θ.
k_1 = velocity constant of first reaction.
k_2 = velocity constant of second reaction.

The differential equations for the separate reactions may then be written

$$\frac{dx}{d\theta} = k_1 c \qquad \text{and} \qquad \frac{dy}{d\theta} = k_2 c \tag{46}$$

These equations contain the four variables x, y, c, and θ. But x, y, and c are related in virtue of the fact that

$$x + y + c = c_0, \text{ the original amount of the parent.} \quad (47)$$

The following data were obtained:

When		
	$\theta = 0$	3 days
	$c = 10$	5 units
	$x = 0$	4 "
	$y = 0$	1 "

It is required to find the values of k_1 and k_2 and to express x, y, and c as functions of the time θ.

Solution. An easy way to begin is to divide the two differential equations one by the other, so as to eliminate $d\theta$. This gives

$$\frac{dy}{dx} = \frac{k_2}{k_1} \quad (48)$$

By separating variables this is the same as $dy = \frac{k_2}{k_1} dx$. Integrating, and noticing that y is zero when x is zero, it follows that

$$y = \frac{k_2}{k_1} x \qquad \text{or} \qquad \frac{y}{x} = \frac{k_2}{k_1} \quad (49)$$

that is, *the ratio of the two products of the process is constant and equal to the ratio of the velocity constanis,* a characteristic property of " side reactions " when the two or more simple reactions are of the same type, known as " Wegscheider's principle." This principle is very important, since it helps in practice to distinguish side reactions from reversible or consecutive reactions, to be considered later. Now since $x = 4$ when $y = 1$ we must have

$$k_1 = 4\, k_2 \quad (50)$$

An easy next step is to add the two differential equations (46), giving

$$\frac{d\,(x+y)}{d\theta} = (k_1 + k_2)\,c \tag{51}$$

but by differentiating (47)

$$d\,(x+y) = -\,dc \tag{52}$$

whence (51) becomes

$$\frac{dc}{d\theta} = -\,(k_1 + k_2)\,c \tag{53}$$

which is of the form (1). In other words the parent substance is used up as if the process were a simple first order reaction with velocity constant equal to the sum of the actual velocity constants. Therefore an equation of the form (15) may be at once written down, namely

$$k_1 + k_2 = -\left(\ln\frac{c}{c_0}\right) \div \theta = -\ln\frac{5}{10} \div 3 = \frac{1}{3}\ln 2 \tag{54}$$

By (50) it follows that k_1 and k_2 are respectively $\frac{4}{5}$ and $\frac{1}{5}$ their sum. Hence $k_1 = \frac{4}{5}\cdot\frac{1}{3}\ln 2 = \frac{4}{15}\,(0.693) = 0.185$ and $k_2 = 0.046$.

The easiest way to express c as a function of θ is to use the " three-point " formula (11),

$$c = 10\left(\frac{1}{2}\right)^{\frac{\theta}{3}} \tag{55}$$

Finally we see from (47) that $x + y = 10 - c$ and from (49) that x and y are respectively 4/5 and 1/5 of their sum. Hence

$$x = \frac{4}{5}\left[10 - 10\left(\frac{1}{2}\right)^{\frac{\theta}{3}}\right] \quad \text{and} \quad y = \frac{1}{5}\left[10 - 10\left(\frac{1}{2}\right)^{\frac{\theta}{3}}\right] \tag{56}$$

Example (*J*). In preparing dinitrobenzene from mononitrobenzene by the addition of nitric acid, it was found experimentally that, when three equivalents of nitric acid were used to one of nitrobenzene at the start, the nitrobenzene was half used up at the end of twenty minutes, and that, at that time, the ortho-, meta-, and para- forms of the dinitrobenzene were present in the proportions of 6.4, 93.5, and 0.1 parts, respectively. The reaction for the formation of each of these three substances is of the second order, the rate being proportional both to the concentration of the nitrobenzene and to the concentration of the nitric acid. Required to find the three velocity constants.

Let c = no. equivalents nitrobenzene left at time θ
c' = no. equivalents nitric acid left at time θ
x, y, z = no. equivalents ortho-, meta-, para-products at time θ.

The set of three simultaneous differential equations will hold,

$$\frac{dx}{d\theta} = k_1 cc', \qquad \frac{dy}{d\theta} = k_2 cc', \qquad \frac{dz}{d\theta} = k_3 cc' \tag{57}$$

Furthermore one equivalent of nitric acid is expended for each equivalent of either of the three products formed; and the same is true of the nitrobenzene. Hence

$$c = c_0 - (x + y + z), \quad \text{and} \quad c' = c_0' - (x + y + z) \tag{58}$$

The solution may be carried out much as in Ex. (I). By dividing one of the differential equations by another and integrating it is easy to see that

$$x : y : z = k_1 : k_2 : k_3 = 6.4 : 93.5 : 0.1 \tag{59}$$

Again, by adding the three differential equations (57) and putting $x + y + z = u$ there results

$$\frac{du}{d\theta} = (k_1 + k_2 + k_3)(c_0 - u)(c_0' - u) \tag{60}$$

so that clearly the sum $k_1 + k_2 + k_3$ can be determined by an equation of the form (41), because (60) is of the same form as (39). The calculation is left to the student.

Example (*K*). A certain tank is filled with water. At a given instant two orifices in the side of the tank are opened to discharge the water. The water at the start is 10 feet deep and one orifice is 6 feet below the top while the other one is 8 feet below the top. The coefficient of discharge of each orifice is known to be 0.61. The tank is a right circular cylinder with vertical axis, and is 6 feet in diameter. The upper and lower orifices are 2 inches and 4 inches in diameter, respectively. How long will be required for the tank to be drained down to a depth of 5 feet?

Solution. Call D the depth of water in the tank at any time θ. The head, in feet of water, above the upper orifice will be $D-4$, while the head above the lower orifice will be $D-2$. The discharge from an orifice of this type is known from hydraulics to satisfy the law

$$u = c\sqrt{2gh} \tag{61}$$

where u is the velocity of discharge through the orifice, (that is u is the speed with which a particle of water is moving as it leaves. The constant c is the coefficient of discharge, which in an ideal fluid free from friction and surface tension might be taken as unity in an ideal orifice, but actually is found by experiment to be about 0.61 for ordinary small orifices with sharp edges; g is the acceleration of gravity, 32.2, and h is the head above the orifice in feet. The formula is a statement of the fact that the kinetic energy of the water on leaving is equal to what it would have had if it had fallen freely through the height h, reduced by departure from ideal conditions.

Call the velocity through the upper orifice u_1 and that through the lower u_2. Then

$$u_1 = 0.61\sqrt{2\,(32.2)\,(D-4)}$$

and

$$u_2 = 0.61\sqrt{2\,(32.2)\,(D-2)} \tag{62}$$

The volume of water discharged per second through the two orifices will be u_1A_1 and u_2A_2, respectively, where A_1 and A_2 are the areas of the orifices in square feet.

The change in the depth of water in the tank is equal to the volume of water leaving the tank divided by the cross-sectional area of the tank, therefore

$$-\frac{dD}{d\theta} = \frac{u_1A_1 + u_2A_2}{9\,\pi} \tag{63}$$

where $A_1 = \pi/144$ and $A_2 = \pi/36$. Collecting values and simplifying

$$-\frac{dD}{d\theta} = \frac{0.61\,\sqrt{64.4}}{9\,(144)}\left[\sqrt{D-4} + 4\,\sqrt{D-2}\right] \tag{64}$$

whence the time for D to fall from 10 to 5 feet is determined by

$$-\int_{10}^{5} \frac{dD}{\sqrt{D-4} + 4\,\sqrt{D-2}} = 0.00378 \int_0^{\theta} d\theta \tag{65}$$

The integral on the left is evaluated by first rationalizing the denominator, (that is, multiplying above and below by $\sqrt{D-4} - 4\,\sqrt{D-2}$), and then separating into the sum of two integrals,

$$-\int_{10}^{5} \frac{\sqrt{D-4}}{28-15\,D}\,dD + 4\int_{10}^{5} \frac{\sqrt{D-2}}{28-15\,D}\,dD = 0.00378\int_0^{\theta} d\theta \tag{66}$$

The calculation may now be completed by the aid of the Hudson-Lipka table of integrals, or by Simpson's Rule.

14. Opposing Processes. — A second very important type of problem arises when two simultaneous processes, instead of occurring independently, tend to oppose or reverse each other.

Example (*L*). A substance C is changed into a second substance X by a reaction of the first order. At the same time X is changing back into C, also by a reaction of the

first order. Observed data:

When			
$\theta =$	0	5	∞
$C =$	10	7	3
$X =$	0	3	7

Find the velocity constants k_1 and k_2 of the two reactions.

Solution. Let c and x denote the equivalents of C and X at time θ. An equation like (18) stated with respect to X is

$$dx = k_1 c\, d\theta - k_2 x\, d\theta \tag{67}$$

This equation contains three variables, but

$$x + c = x_0 + c_0 \tag{68}$$

because the total number of equivalents of both substances is not altered by either reaction. Eliminating c

$$\frac{dx}{d\theta} = k_1 (c_0 + x_0) - (k_1 + k_2)\, x \tag{69}$$

This differential equation has two important properties. First, it is evident from the form of the equation that, as x increases, the rate $\frac{dx}{d\theta}$ will approach zero. In other words, the system will approach a condition of equilibrium as time goes on, a well-known fact.

In the second place, if we adopt the notation (see the remark below)

$$x_\infty = \frac{k_1}{k_1 + k_2} \cdot (c_0 + x_0) \tag{70}$$

and also

$$y = x_\infty - x \tag{71}$$

the differential equation (69) becomes

$$\frac{dy}{d\theta} = -(k_1 + k_2)\, y \tag{72}$$

which means, in words, that the rate of the reaction is proportional to the departure of the system from a state of

equilibrium, and that the process is of the first order with reference to the variable y by which this departure is measured.

That a physical or chemical system may be regarded as activated by the divergence between the state of the system and a state of equilibrium is a principle of wide application.

To find the velocity constants, first find their ratio, by using the observed values in (70). Then find their sum in the usual way from (72). The calculation is left to the student.

Remark on the above solution. The quantity x_∞ defined by (70) is the particular value of x which would cause the right member of (69) to vanish. It is therefore the value which x actually approaches as time goes on. It is also called *the equilibrium value of* x. Similarly in many of the problems which follow, if a variable approaches a limit as time goes on, the subscript ∞ will be used to indicate this limiting value.

In the above example, by eliminating the variable c, we obtained a differential equation (69) which expressed $\frac{dx}{d\theta}$ as a polynomial of the first degree in x, and it appeared in (72) that this polynomial was merely a constant times the factor $x_\infty - x$, here called y.

In general $\frac{dx}{d\theta}$ will be found to be equal to some more complex expression. In many cases which are important in practice, serious algebraic troubles may be avoided by using a principle of which the above is a simple illustration: —

Theorem. If $\frac{dx}{d\theta}$ is equal to a polynomial in the single variable x, (together with constants), and if x approaches a limiting value x_∞ as time goes on, then $x_\infty - x$ is a factor of the polynomial.

This theorem is an application of what is known in al-

gebra as *the factor theorem*, proved in all good text-books of algebra.

In experimental work on reactions or other processes which tend to approach a state of equilibrium, it is important, when possible, to determine by actual measurement, the limiting or equilibrium value of the variable (or variables) on which this state depends. If the experiment is stopped a long way from this final state, it is always difficult, and often quite impossible, to determine accurately velocity constants and related numbers. It may even be impossible to decide on the order of the reaction or the nature of the process. The truth of these statements will appear from a study of the problems which follow.

Example (*M*). Opposing reactions of the second order.

Acetic acid and alcohol react to form acetic ester and water,

$$HC_2H_3O_2 + C_2H_5OH \rightleftharpoons C_2H_5C_2H_3O_2 + H_2O \qquad (73)$$

being of the second order both ways. Observed were

When	$\theta = 0$	64	$\propto$	days
	acid = 1	0.750	0.333	gm. mols.
	alcohol = 1	0.750	0.333	" "
	ester = 0	0.250	0.667	" "
	water = 0	0.250	0.667	" "

Find how many days are needed for the alcohol to fall to half the original amount.

Solution. We shall as usual first set up the general equation for such a process, and obtain a result in which any particular data may be substituted after the integration. Adopt the notation

x, y, u, and v = gm. mols. alcohol, acid, ester, and water at time θ, respectively.

Then the differential equation for the alcohol is

$$\frac{dx}{d\theta} = -k_1xy + k_2uv \qquad (74)$$

To eliminate y, u, and v use the stochiometric relations

$$x_0 - x = y_0 - y = u - u_0 = v - v_0 \tag{75}$$

which are equivalent to

$$y = x + y_0 - x_0, \quad u = x_0 + u_0 - x, \quad v = x_0 + v_0 - x \tag{76}$$

and by virtue of which the differential equation (74) becomes

$$\frac{dx}{d\theta} = ax^2 + bx + c \tag{77}$$

where

$$a = k_2 - k_1, \qquad b = (k_1 - 2\,k_2)\,x_0 - k_1y_0 - k_2u_0 - k_2v_0,$$
$$c = k_2\,(x_0 + u_0)\,(x_0 + v_0) \tag{78}$$

and are constants for any particular run. Now by definition of x_∞

$$0 = ax^2{}_\infty + bx_\infty + c \tag{79}$$

because as x approaches the limiting value x_∞ the chemical system approaches a state of equilibrium and $\frac{dx}{d\theta}$ approaches zero. Subtracting (77) from (79)

$$-\frac{dx}{d\theta} = a\,(x^2{}_\infty - x^2) + b\,(x_\infty - x) \tag{80}$$

the constant c cancelling by subtraction. The right side of (80) factors easily and we have

$$-\frac{dx}{d\theta} = (x_\infty - x)\,(ax_\infty + ax + b) \tag{81}$$

in agreement with the factor theorem. It is best, for reasons soon to appear, to factor out the constant a also, giving

$$-\frac{dx}{d\theta} = a\,(x_\infty - x)\left(x + x_\infty + \frac{b}{a}\right) \tag{82}$$

Much the easiest way, in practice, to handle this differential equation is to notice first that, by setting the right side of

(74) equal to zero (when of course the variables take their equilibrium values), the condition for equilibrium may be written in the form

$$\frac{k_2}{k_1} = \frac{x_\infty y_\infty}{u_\infty v_\infty} \tag{83}$$

The importance of this equation resides in the fact that, if we know the limiting values of the variables, we thereby know the *ratio* of the velocity constants, and furthermore, even if unfortunately we are unable to observe by experiment any one of these limiting values, we shall still make our calculations much simpler by introducing this ratio as one of our unknowns. We shall accordingly represent this ratio by the letter m, namely

$$m = \frac{k_2}{k_1} \tag{84}$$

We now return to the fraction $\frac{b}{a}$ occurring in the second factor on the right of (82). By using the values of a and b from (78) and introducing m by (84) we find

$$\frac{b}{a} = \frac{1}{m-1}\left[(1-2m)\,x_0 - y_0 - mu_0 - mv_0\right] \tag{85}$$

By inspection of this result it appears that if the equilibrium values of the variables be known as well as their initial values, then $\frac{b}{a}$ is known and (82) may be written

$$-\frac{dx}{d\theta} = a\,(x_\infty - x)\,(x+\beta) \tag{86}$$

where

$$\beta = x_\infty + \frac{b}{a} \tag{87}$$

The integration of (86) may now be carried out and the value of a determined in a manner very similar to Ex. (G), for

in *form* (86) resembles the differential equation of a simple second order process. Using the data above given for alcohol and acid we find $k_1 = 4\,k_2$ or $m = \frac{1}{4}$. The differential equation (86) reduces to

$$\frac{dx}{d\theta} = \frac{3\,k_1}{4}\left(\tfrac{1}{3} - x\right)(x + 1) \tag{88}$$

The completion of the work is left as a problem for the student.

It may happen in some special case that $k_1 = k_2$. The constant a is then zero, and cannot be factored out. But (81) reduces to the form of a first order process and presents no difficulty.

Example (N). Reactions of the first order in one direction but of the second order in the reverse direction.

Carbon monoxide decomposes into carbon and carbon dioxide in the presence of a large excess of carbon. The equation is

$$2\,CO \rightleftharpoons C + CO_2 \tag{89}$$

The rate of decomposition of the monoxide is proportional to the square of its concentration, while the reverse reaction proceeds in proportion to the first power of the concentration of the dioxide. These reaction rates are commonly explained, very roughly, by saying that, under the kinetic theory of gases, the rate of any reaction depends on the probability of a collision between the molecules concerned. A more rigorous explanation can be deduced from the laws of thermodynamics, by Gibbs' theory of chemical potentials.

The above statements as to the rate of the reactions are under the assumption that the reaction takes place at constant temperature and constant total volume.

Let x and y be the concentration of CO and CO_2 respec-

tively, at time θ, expressed either in equivalents per unit volume, or in partial pressure as preferred. Then

$$\frac{dy}{d\theta} = k_1 x^2 - k_2 y \tag{90}$$

Now the volume, (or pressure), of CO used up is twice that of the CO_2 formed from it, hence

$$x_0 - x = 2\,(y - y_0) \tag{91}$$

and eliminating y

$$\frac{dy}{d\theta} = k_1 x^2 + \frac{k_2}{2} x - \frac{k_2}{2}\,(x_0 + 2\,y_0) \tag{92}$$

while at equilibrium

$$0 = k_1 x^2{}_\infty + \frac{k_2}{2} x_\infty - \frac{k_2}{2}\,(x_0 + 2\,y_0) \tag{93}$$

so that by subtraction

$$-\frac{dy}{d\theta} = k_1\,(x_\infty - x)\left(x + x_\infty + \frac{k_2}{2\,k_1}\right) \tag{94}$$

If we set

$$m = \frac{k_2}{k_1}, \qquad \beta = x_\infty + \frac{m}{2} \tag{95}$$

we shall have by (90)

$$m = \frac{x^2{}_\infty}{y_\infty} \tag{96}$$

whence m is known from the equilibrium conditions, on which, for most gas reactions, better experimental work has been done than on the rate of reaction. The differential equation takes the form

$$\frac{dx}{d\theta} = 2\,k_1\,(x_\infty - x)\,(x + \beta) \tag{97}$$

and presents no new difficulty.

Example (*O*). Reactions of the second order one way and of the third order in the reverse way. There are a number of gas reactions of this type, for instance

$$2\,CO + O_2 = 2\,CO_2$$
$$2\,SO_2 + O_2 = 2\,SO_3$$
$$2\,H_2 + O_2 = 2\,H_2O$$

Using the first one for an example, (the theory is the same for all), let the concentrations be x, y, and z, for monoxide, oxygen, and dioxide, respectively. Then

$$\frac{dz}{d\theta} = k_1x^2y - k_2z^2 \tag{98}$$

By setting the right side equal to zero

$$m = \frac{k_2}{k_1} = \frac{x^2{}_\infty y_\infty}{z^2{}_\infty} \tag{99}$$

We have also the stochiometric relations

$$x - x_0 = z_0 - z = 2\,(y - y_0) \tag{100}$$

whence, eliminating y and z and introducing x_∞ in the same manner as in the preceding example,

$$\frac{dx}{d\theta} = \frac{k_1}{2}(x_\infty - x)\,(x^2 + bx + c) \tag{101}$$

where

$$b = x_\infty - x_0 + 2\,(y_0 - m), \qquad c = bx_\infty + 4\,m\,(x_0 + z_0) \tag{102}$$

If the initial conditions, as well as the equilibrium conditions, are known, b and c are numbers which can be easily computed. The variables may now be separated,

$$\frac{dx}{(x_\infty - x)\,(x^2 + bx + c)} = \frac{k_1}{2}d\theta \tag{103}$$

The left member is the same as

$$\frac{A\,dx}{x_\infty - x} + \frac{(Bx + C)\,dx}{x^2 + bx + c} \tag{104}$$

where

$$A = B = \frac{1}{x^2{}_\infty + bx_\infty + c} \qquad \text{and} \qquad C = \frac{1-Ac}{x_\infty} \qquad (105)$$

whence A, B, and C are at once calculated and the integration carried out by the aid of the tables.

(For the algebra, see the "method of partial fractions" in any good text book of advanced algebra, or of integral calculus, for example, Hall and Knight's "Higher Algebra" Chap. XXIII. It is easy to verify that, in general, x_∞ is not a root of the quadratic $x^2 + bx + c$. If such were the case, the separation into partial fractions would be slightly modified.)

Any other cases of reversible reactions may be treated in a similar manner, provided the initial and equilibrium conditions are known.

In many processes other than chemical reactions, a variable tends to diminish for one cause and to increase for another cause. The differential equation for this variable is often similar in form to that of a reversible reaction. The following is a simple illustration.

Example (*P*). Suppose the bottom of the tank in example (C) to be covered with a cake of undissolved salt. Assume the surface exposed to be substantially constant, and the salt to dissolve at a rate proportional to the difference between the concentration of the solution and that of a saturated solution, (3 lbs. per gal.). With all other conditions as in example (C), express the total amount of dissolved salt as a function of the time. Given that, if the water in the tank were fresh, one pound of salt would dissolve per minute.

Solution. Equation (18) stated for the dissolved salt is

$$dc = k\,(300-c)\,d\theta - 0.03\,c\,d\theta \qquad (106)$$

We have given that if c were zero then $\frac{dc}{d\theta}$ would be 1 lb. per

min. Hence $k = \frac{1}{300}$. The differential equation may now be written

$$\frac{d\,(c-30)}{d\theta} = -\frac{1}{30}(c-30) \tag{107}$$

whence

$$c-30 = 20\,e^{-\theta/30} \tag{108}$$

showing that the amount of dissolved salt approached 30 lbs. as time goes on (assuming excess of solid salt).

In the preceding examples the data have been, or have been assumed to be, such that the limit approached by the dependent variable could be directly found. If not, the problem is harder, first by reason of the purely mathematical difficulties which arise, second because the data themselves may not suffice. The following example will illustrate one possible method of attack.

Example (*Q*). Diphenyl-chlor-methan reacts in ethyl alcohol yielding hydrochloric acid and an ester. The reaction is assumed to be of the form

$$\mathrm{RCl} + \mathrm{R'OH} \rightleftharpoons \mathrm{HCl} + \mathrm{ROR'} \tag{109}$$

It is desired to verify this assumption, and to determine the velocity constants. The following data were obtained,

When θ =	13	119	142	162	182	212 minutes
HCl =	0.00346	0.02680	0.0309	0.0343	0.0375	0.0418 formal

It is evident that equilibrium was not even approximately attained.

Let x = mols chlor compound at time θ,
y = mols HCl and also mols ester at time θ.

If the reaction is according to (109) the differential equation must be

$$\frac{dy}{d\theta} = k_1 x - k_2 y^2 \tag{110}$$

where k_1 and k_2 are constants, for the amount of alcohol was so large, (about 21 mols), as to remain substantially constant. In this experiment $x_0 = 0.09966$. By stoichiometry $x + y = x_0$ whence x may be eliminated giving

$$\frac{dy}{d\theta} = k_1 (x_0 - y) - k_2 y^2 \tag{111}$$

As before, let y_∞ be the limiting value of y, so that

$$0 = k_1 (x_0 - y_\infty) - k_2 y^2{}_\infty \tag{112}$$

and by subtraction

$$\frac{dy}{d\theta} = k_2 (y_\infty - y)\left(y + \frac{k_1 + k_2 y_\infty}{k_2}\right) \tag{113}$$

We also have directly from (112)

$$k_1 = \frac{k_2 y^2{}_\infty}{x_0 - y_\infty} \tag{114}$$

and may also write

$$\beta = \frac{k_1 + k_2 y_\infty}{k_2} = \frac{x_0 y_\infty}{x_0 - y_\infty} \tag{115}$$

so that both k_1 and β can be determined if y_∞ is known. The differential equation (113) now takes the form

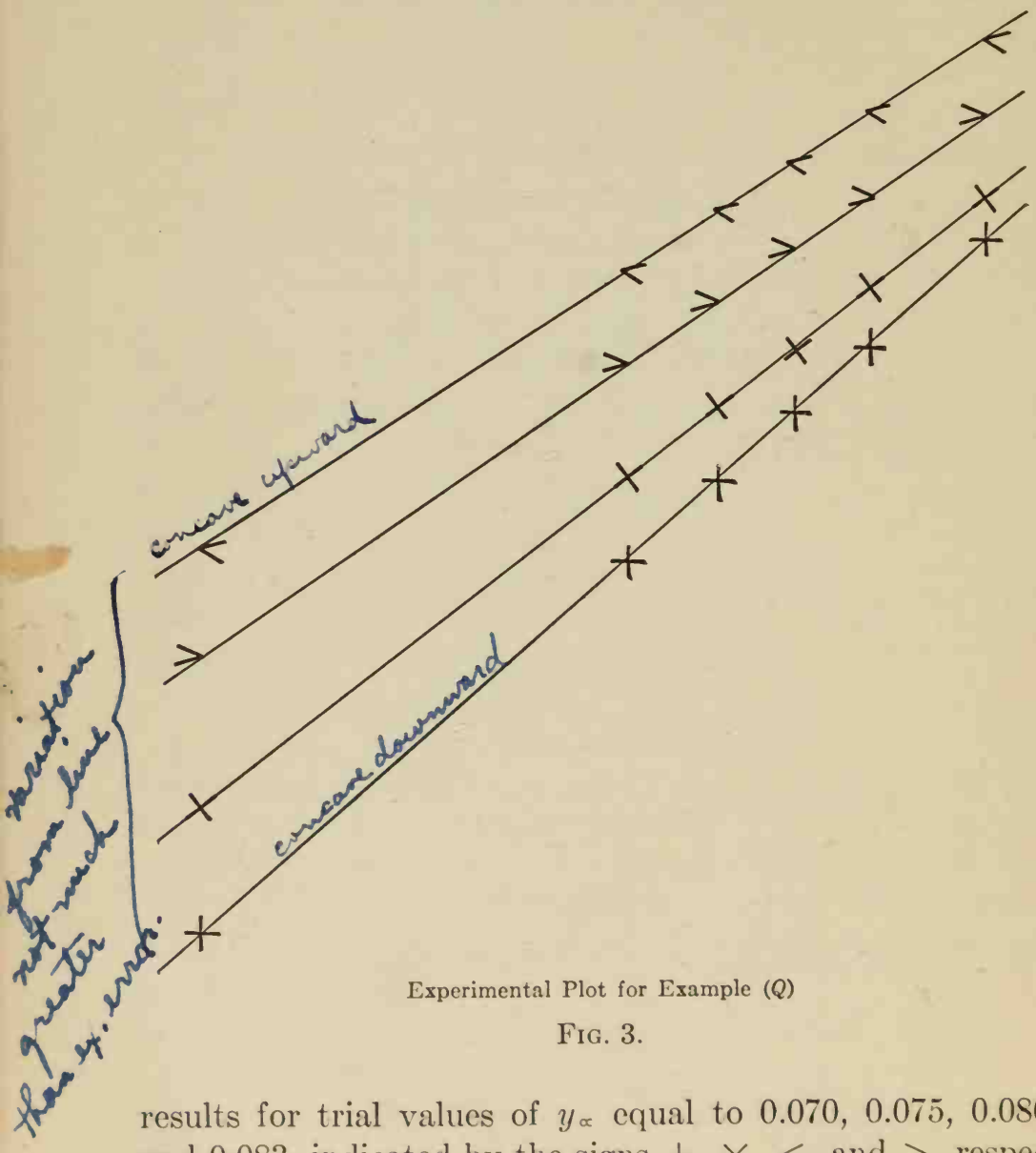
$$\frac{dy}{d\theta} = k_2 (y_\infty - y) (y + \beta) \tag{116}$$

of which the integral may be written

$$\ln \frac{y + \beta}{y_\infty - y} - \ln \frac{\beta}{y_\infty} = (\beta + y_\infty) k_2 \theta \tag{117}$$

The method consists in now assuming a value for the unknown y_∞, and plotting the quantity $\log \frac{y + \beta}{y_\infty - y}$ against θ on ordinary cross-section paper, when, if the true value of y_∞ has been selected, and if the hypothesis as to the

nature of the reaction is correct, the result should be a series of points as nearly on a straight line as the accuracy of the experimental work will justify. Fig. 3 shows the



Experimental Plot for Example (Q)

FIG. 3.

results for trial values of y_α equal to 0.070, 0.075, 0.080, and 0.083, indicated by the signs $+$, $\times$, $<$, and $>$, respectively. The first and the last trials indicate a very slight concavity upward and downward, respectively although the departure from a straight line is in every case comparable

in order of magnitude with the experimental errors. Values of k_2 estimated for the four trials were 0.0170, 0.0118, 0.0082, and 0.0064. Thus the first is more than double the last.

The only conclusion to be drawn with regard to k_2 from such a set of data, (very good in themselves but not carried far enough,) is that, if the reaction is of the assumed form, the constant k_2 probably lies within or very near the interval from the largest to the smallest value obtained. The nearer the experiment is carried to equilibrium, the more accurately k_2 can be estimated by this method, for the differential equation shows that k_2 is more important the larger y becomes.

With k_1 it is quite another story, and the above data suffice to determine its value very well, because k_1 is the predominating constant at the beginning of the reaction. In fact all four trials yield nearly the same value of k_1. The verification is left to the student.

The above data were obtained by a student who was primarily concerned with k_1. In a later experiment with the same substances to determine k_2, a full series of observations, extending to equilibrium, was made by Mr. A. A. Morton of the Massachusetts Institute of Technology, through whose courtesy we are able to publish the results. These will be found in problem 16 below.

15. Consecutive Processes. A third fundamental type of process may be viewed as the result of two simpler processes taking place in succession.

Example (*R*). Suppose a substance of initial amount c_0 changes into a first product, which in turn changes into a second product, the rates of the two reactions being in general different. (Such reactions are very common, the changes, for example, of radioactive substances are of this character universally, so far as is known.) Suppose both reactions to be of the first order.

Let c = amount of parent substance at time θ.
x = amount of first product FORMED up to time θ.
y = amount of second product formed up to time θ.
Then $x - y$ = amount of first product PRESENT at time θ.
The differential equations for x and for y will then be

$$\frac{dx}{d\theta} = k_1 (c_0 - x) \qquad \text{and} \qquad \frac{dy}{d\theta} = k_2 (x - y) \tag{118}$$

because, by hypothesis, x increases at a rate proportional to the value of c, that is $c_0 - x$, while y increases at a rate proportional to the value of the first product actually present, that is $x - y$. The first of these differential equations, since it contains only one dependent variable, can be at once integrated, giving

$$x = c_0 (1 - e^{-k_1\theta}) \tag{119}$$

This value of x is now substituted in the second differential equation. The result is

$$\frac{dy}{d\theta} + k_2 y = k_2 c_0 (1 - e^{-k_1\theta}) \tag{120}$$

a differential equation " linear " in the dependent variable y.

The easiest way to solve a linear equation is to write it in the form

$$\frac{dy}{d\theta} + Py = Q \tag{121}$$

and then to set

$$R = e^{\int P d\theta} \tag{122}$$

when the solution will be given by

$$yR = \int RQ d\theta + \text{const.} \tag{123}$$

as may be easily verified by taking the value of y from (123), putting it back in (121), and showing that the two sides become identically equal.

In the present example $P = k_2$ so that $R = e^{k_2\theta}$ and (123) becomes

$$ye^{k_2\theta} = \int e^{k_2\theta} k_2 c_0 (1 - e^{-k_1\theta})\, d\theta + \text{const.}$$

$$= c_0 e^{k_2\theta} + \frac{c_0 k_2}{k_1 - k_2} e^{(k_2 - k_1)\theta} + \text{const.} \qquad (124)$$

To determine the constant of integration, we have $y = 0$ when $\theta = 0$. Hence

$$0 = c_0 + \frac{c_0 k_2}{k_1 - k_2} + \text{const.} \qquad (125)$$

so that the constant is equal to $-\frac{c_0 k_1}{k_1 - k_2}$ by simplifying. Substituting this value of the constant in (124), and dividing both sides by $e^{k_2\theta}$

$$y = c_0 + \frac{c_0 k_2}{k_1 - k_2} e^{-k_1\theta} - \frac{c_0 k_1}{k_1 - k_2} e^{-k_2\theta} \qquad (126)$$

an important equation because it shows the manner in which the final product of a pair of first order consecutive processes builds up.

It is sometimes possible to make a separate or independent study of the two reactions and thus find the velocity constants k_1 and k_2. This is not always convenient. We shall now suppose that the parent substance was originally pure, and call its amount unity, that is $c_0 = 1$. Suppose also that a complete analysis of a sample was made at a known time θ giving at that time an amount 0.4 of the first product actually present, 0.3 of the second product, and hence of course 0.3 of the parent substance unchanged. Suppose $\theta = 3$. That is, we have found by actual analysis when $\theta = 3$ that $x - y = 0.4$ and $y = 0.3$. We shall show how the "transcendental" equation (126) may be solved for the velocity constants.

In the first place, k_1 may be regarded as known, for the first reaction is a simple first order process, and k_1 is directly found by an equation like (7), Chapter I.

We then must solve (126) for the unknown quantity k_2. We arrange the equation with the exponential term $e^{-k_2\theta}$ alone on one side, at the same time getting rid of the other exponential term $e^{-k_1\theta}$ by putting in its place its value from (119). As a result, (126) takes the much simpler form

$$e^{-k_2\theta} = k_2 \cdot \frac{y - x}{c_0 k_1} + 1 - \frac{y}{c_0} \qquad (127)$$

where by hypothesis all the constants are known except k_2. We then take a small piece of ordinary plotting paper and make a graph of the function $e^{-k_2\theta}$ regarding k_2 as the variable. That is, by assigning a series of values to k_2, we find $e^{-k_2\theta}$ by aid of a table of exponentials and plot $e^{-k_2\theta}$ as ordinate against k_2 as abscissa. The value of θ is kept constant, and is the value at the time the analysis was made. The result is of course a curve of very familiar character.

We next plot the right side of (127) in a similar manner. It is obvious that the result is a straight line, so that it is sufficient to find two or three points, calculating the right side of (127) for ordinates to match selected values of k_2 as abscissa, drawing a line through these points with a ruler. It will in general be found that this straight line cuts the curve already drawn for $e^{-k_2\theta}$ in two distinct points. One of these, if the graphs have been carefully made, will have for its abscissa a value precisely equal to the value of k_1 already found. The other point will have for its abscissa the value of k_2 required in the problem.

The reason k_1 also appears as an intersection is that equation (127) actually has two solutions, one of which is given by setting $k_2 = k_1$, a fact easy to verify directly from (127). The solution $k_2 = k_1$ is " extraneous " and was introduced

when (126) was cleared of fractions to obtain (127), because it was necessary to multiply by $k_1 - k_2$. This extra point of intersection is a help, not a hindrance, because if we know that the line and the exponential curve intersect when $k_2 = k_1$ we have a check on the draughtsmanship.

If in a particular case it should really be true that $k_2 = k_1$, the straight line would be precisely tangent to the exponential curve. When the value of k_2 has been approximately found from a first graph, a more accurate value may be found by plotting on a larger scale a portion of both the curve and the line in the required region. Thus k_2 may be found as closely as needed.

Applying this method to the data above assumed to be known, we have first $k_1 = -\frac{1}{3} \ln (0.3) = 0.40$ and then (127) becomes

$$e^{-k_2(3)} = -k_2 + 0.7 \qquad (128)$$

By plotting, it is easily found that k_2 is near the value 0.35. As a final determination, a few values may be tabulated from a table of natural logarithms, thus

$$\ln 0.35 = -1.04982,\ k_2 = -\tfrac{1}{3} \ln 0.35 = 0.34994,\ -k_2 + 0.7 = 0.35006$$

$$\ln 0.355 = -1.03564,\ k_2 = -\tfrac{1}{3} \ln 0.355 = 0.34516,\ -k_2 + 0.7 = 0.35484$$

In the first line, we have taken the value of e^{-3k_2} to be 0.35, giving the right side of (128) as 0.35006, which is larger than 0.35.

In the second line, we have assumed the left side to be 0.355, giving the right side as 0.35484, which is smaller than 0.355. Hence k_2 is between 0.34994 and 0.34516. This method may be used to check or to replace the graphic method, which is illustrated by Fig. 4.

If k_1 is not very different from k_2, the straight line will be nearly, but not quite, tangent to the curve, and will run

nearly parallel to the curve near the desired point. We may, however, largely overcome this difficulty by greatly increasing the scale of measure on the vertical axis, for the

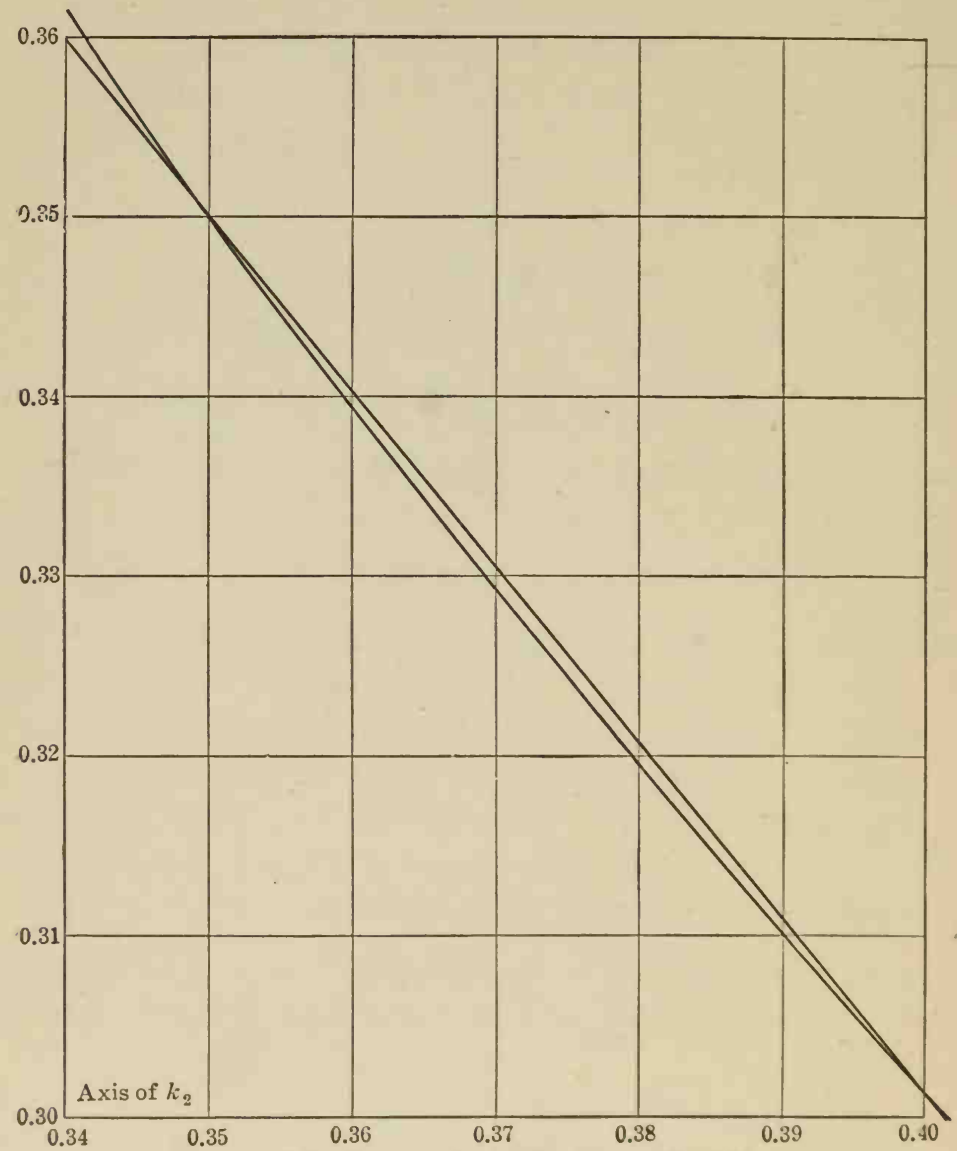


FIG. 4.

curvature of the curve is exaggerated while the line remains straight. In such cases, however, the method of numerical tabulation is to be preferred. In all cases a rougher graph

should first be made to determine the approximate value of k_2.

Example (*S*). Show that in a pair of consecutive first order processes the first product rises to a maximum and then falls off toward zero. Find the maximum amount of this first product, and the time when the maximum is reached.

Solution. Subtracting (126) from (119) and simplifying

$$x - y = \frac{c_0 k_1}{k_2 - k_1}[e^{-k_1\theta} - e^{-k_2\theta}] \tag{129}$$

Differentiating with respect to θ we have

$$\frac{d\,(x - y)}{d\theta} = \frac{c_0 k_1}{k_2 - k_1}[-k_1 e^{-k_1\theta} + k_2 e^{-k_2\theta}] \tag{130}$$

If we were to plot the graph of $x - y$ against θ, equation (130) shows that the slope at the start must in all cases be $c_0 k_1$, because the right side reduces to this value when $\theta = 0$. To find the maximum we set the right side equal to zero, giving

$$\frac{k_1}{k_2} = e^{(k_1 - k_2)\theta} \tag{131}$$

which solved for θ gives

$$\theta = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2} \tag{132}$$

as the time when the first product attains its maximum amount. For example, if it were desired to obtain the greatest possible yield of this first product, (132) gives the proper time to stop the operation.

To find the value at the maximum, set, in (129),

$$e^{-k_2\theta} = \frac{k_1}{k_2} e^{-k_1\theta} \tag{133}$$

because the right side of (130) is zero at the maximum. Then (129) simplifies to

$$x - y = \frac{c_0 k_1}{k_2} e^{-k_1\theta} \tag{134}$$

at the maximum of $x - y$. The value of θ from (132) is now used, and (134) reduces to

$$x - y = c_0 \left[\frac{k_1}{k_2}\right]^{\frac{k_2}{k_2 - k_1}} \tag{135}$$

as the maximum yield of the first product.

It is evident that the form of the above investigation would require modification in case k_1 is substantially equal to k_2. This case is left as a problem for the student.

16. Processes of Mixed Type. — The three types which have been studied in this chapter, side by side, reversible, and consecutive, very commonly occur together. The number of possible combinations is very large, but methods in general similar to the foregoing may be used to set up the differential equations, — which, however, are not necessarily either separable or linear.

The following simple but important example will serve as an illustration.

Example (*T*). Steam was passed over heated carbon, yielding " water gas," which is a mixture of steam, carbon dioxide, carbon monoxide, and hydrogen. Reckoned on a basis of one unit volume of pure steam at the start, the following results were obtained:

When volume of steam =	1.000	0.906	0.709	0.556	0.376	0.056
volume of CO_2 =	0.000	0.041	0.100	0.123	0.099	0.0242

Show that these results are in good agreement with the hypothesis that the reactions are

(A) $C + 2\,H_2O = CO_2 + 2\,H_2$

(B) $C + H_2O = CO + H_2$

(C) $C + CO_2 = 2\,CO$

together with the hypotheses that all three reactions are of

the first order and that none of them are reversible to a perceptible extent under the conditions of the experiment.

Also determine the RATIOS of the velocity constants.

Solution. Let k_1, k_2, and k_3 be the velocity constants of the respective reactions. The carbon dioxide is formed in (A) and used up in (C). Letting x and y denote the volumes of steam and of CO_2 at time θ, the differential equation for y will be, on the above hypotheses,

$$\frac{dy}{d\theta} = k_1 x - k_3 y \tag{136}$$

Again, the steam is used up in both (A) and (B), these two being side reactions, while (C) is consecutive. In writing (136) the constant k_1 was chosen to correspond to the rate of formation of one volume of CO_2, corresponding to two volumes of steam. The differential equation for the steam will thus be

$$\frac{dx}{d\theta} = -2\,k_1 x - k_2 x \tag{137}$$

Since it was not practicable to observe the values of θ, we divide the two differential equations to eliminate $d\theta$. The result is

$$\frac{dy}{dx} = \frac{k_1 x - k_3 y}{-2\,k_1 x - k_2 x} \tag{138}$$

If we divide numerator and denominator by k_1 and, for simplicity, adopt the notation

$$\beta = \frac{k_3}{k_1} \qquad \text{and} \qquad \alpha = 2 + \frac{k_2}{k_1} \tag{139}$$

the equation (138) takes the form

$$\frac{dy}{dx} = \frac{\beta y - x}{\alpha x} \tag{140}$$

This equation is linear in y and may be integrated as in

the previous example. The values of α and β may then be found by trial, hence the ratios k_3/k_1 and k_2/k_1 are known. The computation is left to the student.

Remark on the above solution. We might perhaps expect reaction (A) to be of the second order, a hypothesis which leads to a differential equation not in agreement with the data. We must remember, however, that this reaction takes place on the surface of the carbon, so that we should not reason by analogy with gas reactions. For a full discussion, with many more data, see a paper by Haslam, Hitchcock, and Rudow, in "Industrial and Engineering Chemistry," Feb., 1923. It is of both theoretical and practical interest that data over a wide range of pressure, and also of temperature, agree with the equation (140).

PROBLEMS

1. A substance c yields two products x and y. The following observations were made:

When θ =	0	5
c =	10	7
x =	0	2
y =	0	1

Find the velocity constants, assuming two side reactions of the first order. Does it matter in this problem whether the substances are measured in grams or in gm. mols?

2. Complete the calculations in Ex. (J).

3. Complete the calculation in Ex. (K).

4. Set up and integrate the differential equations for a pair of side reactions, one of which is of the first order, the other of the second. Does Wegscheider's principle hold?

5. Complete the calculations in Ex. (L).

6. It was shown by P. Henry that gamma-oxy-butyric acid is converted into gamma-butyrolactone at the following rate:

When θ = 0	50	100	220	∞
lactone = 0	4.96	8.11	11.55	13.28

The initial amount of acid was 18.23. Show that these data are in

agreement with the hypothesis that the reaction is reversible and of the first order both ways.

Hint: plot $x_\infty - x$ against θ on semi-log paper.

7. Find the velocity constants in Prob. 6.

8. Complete the calculations in Ex. (M), finding also the values of the velocity constants.

9. How long would it have taken in Ex. (M) for the alcohol to fall to half its value if we had started with three equivalents of acid to one of alcohol, other conditions remaining such that the velocity constants are the same as before? Find also the amounts of the four substances present when equilibrium is reached.

10. By experiment it is known that when carbon, carbon monoxide, and carbon dioxide are in equilibrium at 900° C. the partial pressure of the dioxide is 0.0232 times the square of the partial pressure of the monoxide. Assuming that the experiment started with pure CO in presence of excess of carbon, and adopting as unit of time the interval required for the CO to diminish by one tenth of one per cent, find the time required for the CO to fall to the value midway between its initial value and its equilibrium value. Assume one unit of pressure at the start.

11. With the data of Ex. 10, assume that the experiment started with pure CO_2 in presence of excess of carbon. Adopt as unit of time the interval required for the CO_2 to diminish by one tenth of one per cent. Find the time required for the CO_2 to fall to the value midway between its initial value and its equilibrium value. Assume one unit of pressure at the start.

12. What is the ratio of the time units employed in Probs. 10 and 11? Are the velocity constants the same in these two problems? Explain.

13. Find the per cent analysis of the equilibrium gases in Probs. 10 and 11. Would the number 0.0232 have to be altered if we altered the unit of pressure? Do you know the unit of pressure actually employed in this experiment?

14. With all other conditions as in Ex. (P), assume the water in the tank to be fresh at the start. Express the total amount of dissolved salt as a function of the time. What limit is approached as time goes on? Compare your answer with that of Ex. (P).

15. A square tank is originally filled with water to a depth of 6 ft., but an orifice two ins. in diameter is opened in the bottom. To make up the loss, water is let into the top of the tank at a constant rate, after which it is observed that the water level falls to four ft. and remains constant. How fast is the water coming in at the top?

16. Diphenyl-chlor-methan reacts with excess of alcohol as in Ex. (Q). The following data were obtained:

The chlor compound at the start was 0.08808 formal.

When θ =	1	3	5	8	10	16
HCl =	0.001520	0.001979	0.002455	0.003098	0.00367	0.00484
When θ =	21	26	31	41	51	61
HCl =	0.00586	0.00693	0.00795	0.00994	0.01190	0.01387
When θ =	63	82	103	125	151	175
HCl =	0.01430	0.01860	0.02135	0.02492	0.02855	0.03246

When θ = 1037 $\propto$ minutes
HCl = 0.07179 0.07405 formal

The value of the HCl for $\theta = \propto$ was obtained by allowing the experiment to proceed until the HCl remained constant at 0.07405 for two days in succession.

Show that this run is consistent with the hypothesis that the reaction is of the first order in one direction, and of the second order in the reverse direction, as in Ex. (Q). Find the velocity constants.

17. From the data of Ex. (Q) find k_1. Compare with Prob. 16. Should the values of k_1 from Ex. (Q) and from Prob. 16 be expected to agree? How ought they to be compared? If the alcohol had not been in excess what changes would you make in the method of calculation?

18. Study the following runs with the object, first, of finding whether the reaction has the form and character assumed in Ex. (Q), and second, of finding the velocity constants.

Run (*a*). P-methyl diphenyl chlor methan in ethyl alcohol.

Initial solution of chlor-compound was 0.09690 formal.

When θ =	10	14	18	22	30	41	52	68
HCl =	0.0348	0.0439	0.0503	0.0547	0.0606	0.0642	0.0659	0.0668

Run (*b*). O-chlor diphenyl chlor methan in ethyl alcohol.

Initial solution of chlor-compound was 0.09730 formal.

When θ =	18	49	93	159	209	251	339
HCl =	0.00014	0.00022	0.00032	0.00048	0.00061	0.00071	0.00091

When θ = 400 953 minutes
HCl = 0.00105 0.00229 formal

Run (*c*). Diphenyl chlor methan and isopropyl alcohol.

Initial solution of chlor-compound 0.09970 formal

When θ =	45	74	106	134	165	225	958 minutes
HCl =	0.0012	0.0020	0.0028	0.0036	0.0044	0.0059	0.0212 formal

Run (*d*). P-phenyl diphenyl chlor methan in ethyl alcohol.

Initial solution 0.02463 formal.

When θ =	11	21	30	43	55	77	94	125
HCl =	0.0075	0.012	0.015	0.0179	0.0195	0.0212	0.0217	0.0222

19. Find the velocity constants in Prob. 1, assuming that the reactions are consecutive instead of side by side. Assume x to be the first product and y to be formed from x, both reactions being of the first order, and not reversible. $K_1 = .0713$ $K_2 = 1.575$

Caution. Note that x, the amount of the first product PRESENT corresponds to the quantity $x - y$ of Ex. (R).

20. Find the velocity constants in Prob. 1, assuming that the reactions are consecutive instead of side by side. Assume y to be the first product, and x to be formed from y, both reactions being of the first order and not reversible.

Caution. Note that y, the amount of the first product PRESENT corresponds to the quantity $x - y$ of Ex. (R), and that x, the amount of the second product present, corresponds to y of example (R).

21. Using the results of Prob. 1, plot two curves showing the amount of each product as ordinate against time as abscissa.

22. Using the results of Prob. 19, plot two curves showing the amount of each product present at time θ.

23. Using the results of Prob. 20, plot two curves showing the amount of each product present at time θ.

Compare carefully the graphs of Probs. 21, 22, 23. Suppose we are able by chemical analysis to determine one product at any time, but are unable to determine a second product directly, can we always decide whether the reactions are consecutive or side-by-side? If consecutive, can we decide which is the first product?

24. Using the results of Prob. 19, calculate accurately the time when x is a maximum, and find the value of this maximum. Check by the graph of Prob. 22.

25. Uranium changes into radium by a first order process. Radium also decomposes by a first order process. If we started with a given amount of pure radium, this amount would fall to half its value in about ~~1300~~ 1900 years. In ancient rocks the ratio of the amount of uranium

to that of radium is 3,200,000 to one. How long a time would be needed for a given amount of uranium to fall to half its value?

Some rocks are actually well over 50% uranium. State carefully just what can be deduced as to the age of these rocks, on the basis of the above facts.

26. Determine the ratios of the velocity constants in Ex. (T).

27. Steam was passed over heated carbon, yielding water gas, the temperature being much higher than in Ex. (T). The following data were observed,

When vol. of steam =	1.000	0.788	0.725	0.532	0.340	0.255	0.110
vol. of CO_2 =	0.000	0.061	0.065	0.126	0.093	0.067	0.021

Show that these results are in approximate agreement with the assumptions of Ex. (T) and find the ratios of the velocity constants. Is the slight departure from the assumptions of Ex. (T) progressive or accidental? If not accidental, on what hypothesis may it be explained?

28. Mustard gas (M) suffers hydrolysis in presence of excess of water, yielding an intermediate compound (I) and hydrochloric acid which is of course dissociated into ions H^+ and Cl^-. The intermediate compound reacts with more water yielding a final product (G) and more hydrochloric acid. The reactions may be written

$$(M) + H_2O = (I) + H^+ + Cl^-$$
$$(I) + H_2O = (G) + H^+ + Cl^-$$

but it is conceivable that either one of these reactions may be reversible.

The following further facts are known:

1°. As time goes on, the mustard gas is completely converted into (G), the amounts of both (M) and (I) approaching zero as a limit.

2°. The net rate of hydrolysis is retarded by the addition of acids.

3°. The second reaction under all circumstances proceeds very rapidly in the direction of the formation of (G).

With dependent variables (M), (I), (G), (H^+) and (Cl^-), set up a pair of differential equations corresponding to the pair of reactions. Write down also three stoichiometric relations by means of which three of these variables can be eliminated. Which variables are best to eliminate?

The resulting pair of simultaneous differential equations need not be integrated.

CHAPTER V

EQUATIONS OF FLOW

17. Continuous and Intermittent Processes. In the preceding chapters have occurred a number of problems on flow. While typical and important, these have been mathematically of a fairly simple character, because the concentrations of the substances concerned were assumed to be constant throughout the tank, gas-flask, or recitation room at a given instant of time. The flow was taken to be slow enough so that the incoming current could mix thoroughly with the material present. The differential equation of the process was therefore concerned only with the time-change of concentration in the system as a whole.

There is another type of process which is just the opposite: the concentration of any material is constant at a fixed point in the system, in the sense that at that point the conditions do not change at all with time, but as we travel from point to point in the apparatus we find a change of condition. A process of this kind is known as " continuous " because it can be carried on for an indefinite period without interruption. The state of the system is known as " steady," implying no time-change at any given point. The differential equations corresponding to a continuous process will be characterized by the absence of partial derivatives with respect to time taken at a fixed point. The independent variable will usually be the distance a particle of material has traveled since entering the apparatus, or some quantity of similar nature defining position in the system.

A typical example of what is meant by a continuous process is afforded by Example (V), below, where the wet

clay is fed into the upper end of a cylinder at a substantially constant rate, while the dry clay falls out at the lower end, the water being carried away by a steady current of air flowing in the opposite direction. The conditions at any one point in the drier are constant, that is, the state is steady. The mathematics of a steady state is usually not difficult. In the case of the drier just mentioned, we follow the history of a definite portion of clay in its journey through the drier, using as independent variable either the distance it has traveled since entering, or the time it has been on the way, as we may prefer. For dependent variables we shall have such quantities as the humidity of the clay, its specific gravity, the humidity of the air in contact with it, and so on. If we remained at a fixed point in the drier, we should observe no changes at all or, as above remarked, time derivatives at that point would be zero, because the state is steady.

In processes of the most general type, one or more of the variables will change both in time and in space. A process which is not continuous is said to be " intermittent." If clay were placed in a loft, and a current of air were driven over it until all moisture had been extracted, the clay being then replaced by a fresh batch, the process would be intermittent. It would clearly not be a continuous process with respect to the clay, nor yet with respect to the air current, which would gather moisture more rapidly in the early stages.

If the state of some variable is " steady," there will be no time derivatives of that variable taken at a *fixed point*, or to say the same thing in a more mathematical way, the *partial derivative* of that variable with respect to time will be zero. On the other hand, *if we travel along with a portion of the material*, that variable will in general change, that is, its *total derivative* with respect to time will not be zero.

The occurrence of partial derivatives makes some of these

processes more difficult in a mathematical sense. In many cases, however, there are simplifying circumstances which make it possible to handle the resulting equations. In the present chapter we shall first illustrate the general method of setting up the differential equations of a process involving flow, and shall afterwards give examples of the simplifying circumstances in a variety of cases.

18. Illustrations of the General Method. The logic employed is essentially the same as that of the first and simplest problem on flow which we had, namely Example (C), and consists merely in setting down in mathematical language the fact that matter is not created or destroyed. Considering a definite portion of space, this consists in saying that all material which enters the space must either stay there or pass out. More mathematically, the rate at which a particular substance increases within that space is equal to its rate of income minus its rate of output, which is equation (18) under Example (C).

The portion of space usually considered in setting up the equation of continuity (18) is that bounded by two sections of the apparatus at the two points x and $x + dx$, where x is the distance from the entrance to the drier, tube, or other apparatus.

Example (*U*). Assume a compressible gas flowing through a long straight tube of uniform cross-section, and undergoing a change of density during its passage through the tube due to a drop in static pressure or other cause.

Let

u = velocity of flow at any point x at any time θ.
ρ = density of the gas at point x and time θ.
A = cross-section of the tube, a constant.

We may suppose the units employed to be feet, pounds, and seconds.

The mass of gas passing the point x per second is the

product of the velocity, the density, and the cross-section A, that is $A\rho u$.

The mass of gas passing the point $x + dx$ will be $A\,[\rho u + d\,(\rho u)]$.

The difference between these two expressions, that is $-\,A\,[d\,(\rho u)]$, will be the rate of accumulation of gas in the space between the points x and $x + dx$. Now if we call ρ' the *average* density of the gas in this space, the actual mass of gas in the space will be $A\rho' dx$, because $A dx$ is the volume of the space and mass is volume times density. The rate of change of this quantity, that is the rate of accumulation of gas in this space, is $\frac{\partial}{\partial\theta}\,(A\rho' dx)$ which is the same as $A dx\,\frac{\partial\rho'}{\partial\theta}$ since A is constant and x is independent of θ.

Equating the two values just found for the rate of accumulation,

$$-\,A d\,(\rho u) = A dx\,\frac{\partial\rho'}{\partial\theta} \tag{141}$$

We now cancel A, divide by dx, and let dx approach zero. The average density ρ' approaches ρ as a limit, and the quotient $\frac{d\,(\rho u)}{dx}$, as dx approaches zero, approaches the partial derivative $\frac{\partial\,(\rho u)}{\partial x}$, because the distance dx was an increment in x taken independently of the time θ. The above equation thus becomes

$$-\,\frac{\partial\,(\rho u)}{\partial x} = \frac{\partial\rho}{\partial\theta} \tag{142}$$

which is the equation of continuity for this case.

In obtaining this partial differential equation no assumption whatever was made with reference to the character of the flow of the gas through the tube. The process may be either continuous or intermittent. The equation is a

necessary condition for the flow of a compressible gas through a tube of constant cross-section, under the sole limitation that all of the gas which enters the tube must either remain in the tube or pass out, — in other words, it is not destroyed by any chemical process within the tube, or absorbed by the walls of the tube, or in any other way got rid of.

It need hardly be remarked that such an equation is not by itself *sufficient* to enable us to find the dependent variables u and ρ at any point and at any time. To do so, two further pieces of information would be required.

1°. Since there are two dependent variables u and ρ, we shall require, besides equation (142), one further relation of some kind satisfied by u or ρ or both. This relation may or may not consist of a second differential equation.

2°. In general, in order to solve completely a partial differential equation, such as (142), we need to know the values of the dependent variables u and ρ throughout the system for at least one value of the time, (as at the start of the experiment), and need furthermore to know their values at some one point (as at the entrance to the tube) for all values of the time. This statement will naturally require amplification or modification in special cases, and the information here described may frequently be replaced by other facts, which, however, would serve a similar purpose.

As a special case, we may now suppose the process to be "continuous," which is the same as assuming all partial derivatives with respect to time to be zero. The equation (142) becomes

$$\frac{\partial (\rho u)}{\partial x} = 0 \tag{143}$$

or merely $\frac{d (\rho u)}{dx} = 0$, because we have now only one independent variable. Hence

$$\rho u = \text{constant} \tag{144}$$

a simple but important relation for a process of this type.

In this discussion we have used the words " compressible gas," but there is nothing in the reasoning that does not apply equally well to any substance whatever, provided that in reckoning density we make the calculation with respect to that substance alone, neglecting other material, such as moisture, which may have been lost or gained in the process. The next example will serve as illustration.

Example (*V*). A lumpy material is dried in a hollow rotary cylindrical drum 5 feet in diameter and 30 feet long. The drum is substantially one third full of lumps at all points. The axis of the cylinder is nearly but not quite horizontal. The material enters the drum at a constant rate and travels slowly through it by gravity due to the tumbling action obtained by the rotation. The lumps entering contain two thirds water, which amounts to two pounds water per pound of clay reckoned on a water free basis. The clay on leaving the drier contains 0.1 pound of water per pound of clay.

The volume of the clay may be taken to be a linear function of the water it contains. The material entering weighs 31 pounds per cubic foot and leaving 22 pounds per cubic foot.

The drier discharges 550 pounds of material per hour. The rate of evaporation may be taken as proportional to the water content of the material at any point.

Let it be required to set up the equation of continuity for the clay and to find how long it takes the material to pass through the drier.

Solution. We note first that the process is of the continuous type. At the exit, we are told that 550 pounds of material pass out per hour, containing 0.1 pounds of moisture per pound of clay. Therefore 500 pounds of clay pass out per hour. It follows that, because the state is everywhere " steady," 500 pounds of clay per hour pass across any and every section of the drier. If this were not so there would

be an accumulation or piling up of clay contrary to the hypothesis that the state is steady.

We may next let V represent the volume occupied by one pound of clay, reckoned on a water-free basis, (that is of one pound of actual clay, not counting the water which it contains). Let w be the weight of water held by this pound of clay. By hypothesis, V is a linear function of w, that is

$$V = aw + b \tag{145}$$

where a and b are constants.

Also let u = velocity of material at any point x, and A = cross-section of material, which is one third the cross-section of the drier. The density ρ of the clay itself will be $\frac{1}{V}$. The weight of actual clay passing any point per hour will be $u\rho A$, and, as already seen, is equal to 500, hence

$$u\rho A = 500 \tag{146}$$

which is a case of equation (144), the equation of continuity for the clay. To give this the form of a differential equation, set $u = \frac{dx}{d\theta}$ where θ is the time required for a portion of clay to move from the entrance to the point x. Putting also for ρ and V their values we obtain

$$\frac{dx}{d\theta} = \frac{500}{A}(aw + b) \tag{147}$$

This differential equation contains three variables, x, θ, and w. A second differential equation is yielded by the fact that we have assumed the rate of evaporation to be proportional to the moisture content, or

$$\frac{dw}{d\theta} = kw \tag{148}$$

which implies that the air current is rapid enough so that the humidity of the air in the drier may be taken as constant. The values of a and b may be found by using the initial and final states of the clay, as given. The pair of simultaneous differential equations may be integrated without difficulty, and the time of passage through the drier computed. This is left as a problem for the student.

Example (*W*). As a further illustration of the general method of setting up an equation of continuity, let there be a cube of solid material of uniform character, and of initial constant temperature T_1 throughout. Let one face of the cube be placed in contact with a cooler which is kept at the constant temperature T_2. Let the other five faces of the cube be perfectly insulated, so that the heat flowing in or out through them may be neglected. Set up the equation for the flow of heat in the cube.

Solution. Consider a cross-section of the cube parallel to the first face and distant x from it. Call the specific heat of the material s and its density and conductivity respectively ρ and k. Let a denote the length of an edge of the cube. By Newton's law of cooling, the amount of heat Q that crosses an area A perpendicular to the x-axis in unit time is given by

$$Q = -kA\frac{\partial T}{\partial x} \tag{149}$$

where T is the temperature at the point x. The amount which crosses an area at the point $x + dx$ will therefore be

$$-kA\left[\frac{\partial T}{\partial x} + d\left(\frac{\partial T}{\partial x}\right)\right] \tag{150}$$

and the difference between these two expressions,

$$kAd\frac{\partial T}{\partial x} \tag{151}$$

will be the rate at which heat is accumulating between the two sections, by reasoning quite similar to Example (U). Now if T' is the average temperature of the portion of the cube between these two sections, the rate of accumulation of heat in this portion will be

$$s\rho A dx \frac{\partial T'}{\partial \theta} \tag{152}$$

because Adx is the volume, ρAdx is the mass, and hence $s\rho Adx$ is the heat capacity of this portion. Heat capacity multiplied by rate of change of (average) temperature gives rate of heat increase. We now equate our two expressions for rate of heat accumulation, cancel A, divide by dx, and let dx approach zero, precisely as in Example (U). The result is

$$k \frac{\partial^2 T}{\partial x^2} = s\rho \frac{\partial T}{\partial \theta} \tag{153}$$

which is the equation of continuity for one-dimensional heat flow.

This partial differential equation contains only the one dependent variable T. We know the initial state, and the law governing the conditions on the bounding faces of the cube. We shall therefore expect to be able to find the temperature distribution in the cube at a point x and time θ.

The easiest method (when it can be used) for solving a partial differential equation with two independent variables, is to assume a solution of the form yz, where y is a function of one independent variable only and z is a function of the other independent variable only. That is, we may write

$$T = yz \tag{154}$$

where we suppose T to be a particular solution of (153), with y a function of x and z a function of θ. Substituting yz for T in (153) gives

$$kz\frac{d^2y}{dx^2} = s\rho y\frac{dz}{d\theta} \tag{155}$$

and by separation of variables

$$\frac{1}{y}\frac{d^2y}{dx^2} = \frac{1}{z\tau}\frac{dz}{d\theta} \tag{156}$$

where, for compactness, $\frac{1}{\tau}$ has been written for the constant quantity $\frac{s\rho}{k}$. Now the left side of this equation is by hypothesis not a function of θ, and the right side is not a function of x, and since the two sides are equal they must both be free from x and θ, that is, both sides are equal to a constant. Let this constant be $-c^2$, giving

$$\frac{1}{y}\frac{d^2y}{dx^2} = -c^2 \qquad \text{and} \qquad \frac{1}{z\tau}\frac{dz}{d\theta} = -c^2 \tag{157}$$

a pair of ordinary differential equations. A solution of the second is

$$z = e^{-c^2\tau\theta} \tag{158}$$

which shows why we took the constant of the form $-c^2$, for T on the whole will diminish as time goes on so that this constant must be negative. A solution of the other equation is either

$$y = \sin cx \qquad \text{or} \qquad y = \cos cx \tag{159}$$

as can be seen by substitution. To decide between these two, we may, without loss of generality choose a temperature scale (by writing $t = T - T_2$) such that the temperature of the cooler is taken as zero. Thus $t = 0$ when $x = 0$. Then the form $\sin cx$ is alone admissible. Collecting results, we take as a particular solution of (153)

$$t = \sin cx \cdot e^{-c^2\tau\theta} \tag{160}$$

which, it is easy to verify directly, is actually a solution, independent of the value of c. It is also clear that this function is still a solution if we multiply it by any constant.

We may next determine the constant c to agree with the condition that at the face of the cube opposite the cooler, that is when $x = a$, there is no flow of heat. By Newton's law (149) this is the same as saying that the derivative $\frac{\partial t}{\partial x}$ vanishes when $x = a$. From (160)

$$\frac{\partial t}{\partial x} = c \cos cx \, . \, e^{-c^2 \tau \theta} \tag{161}$$

and since the exponential function cannot be zero we must have

$$\cos ca = 0 \tag{162}$$

giving the general solution

$$ca = (2n - 1)\frac{\pi}{2} \tag{163}$$

where n is an integer. Thus c may have any of an infinite number of values. This is a very fortunate circumstance, for we have still to satisfy the condition that the temperature is constant all over the cube when $\theta = 0$. Up to this point the work of solution of the partial differential equation has consisted of a number of very elementary steps of the simplest character from the point of view of computation. There has been nothing in the calculus employed which goes beyond the ordinary formulas of the freshman year. To satisfy the condition that the temperature is constant at the start, while not difficult, is a little less elementary. Note first that if n is an integer then $2n - 1$ is an odd integer. Thus if $n = 1$, $c = \frac{\pi}{2a}$; if $n = 2$, $c = \frac{3\pi}{2a}$; if $n = 3$, $c = \frac{5\pi}{2a}$, and so on. We now assume

$$t = A_1 \sin c_1 x \,.\, e^{-c_1^2 \tau\theta} + A_2 \sin c_2 x \,.\, e^{-c_2^2 \tau\theta} + A_3 \sin c_3 x \,.\, e^{-c_3^2 \tau\theta} + \cdots \quad (164)$$

an infinite series where the successive values of c are those determined by (163).

Each term of the series, from its method of derivation, satisfies the original partial differential equation (153); each term vanishes when $x = 0$; and each term gives a derivative which vanishes when $x = a$. Hence the same properties hold for the whole series. When $\theta = 0$ the exponential factors all reduce to unity, and the series becomes

$$t_0 = A_1 \sin c_1 x + A_2 \sin c_2 x + A_3 \sin c_3 x + \cdots \quad (165)$$

The final step in the solution is to determine the constants A_1, A_2, A_3, $\cdots$ in such a way that t_0 shall equal the constant $T_1 - T_2$, so that the initial temperature of the cube shall be T_1. This is one of the simplest examples of "Fourier's Series." It is known that

$$4\left(\frac{\sin x}{1} + \frac{\sin 3x}{3} + \frac{\sin 5x}{5} + \cdots\right) = \pi \quad (166)$$

when $0 < x < \pi$. (See References below.)

whence comparing coefficients between (165) and (166) we have

$$A_1 = \frac{4}{\pi}(T_1 - T_2), \qquad A_2 = \frac{A_1}{3}, \qquad A_3 = \frac{A_1}{5}, \text{ etc.} \quad (167)$$

By putting these values in (165) we have as the complete solution of the problem

$$T = T_2 + \frac{4}{\pi}(T_1 - T_2)\left(\sin \frac{\pi x}{2a} \cdot e^{-\frac{\pi^2 \tau\theta}{4a^2}} + \frac{1}{3} \sin \frac{3\pi x}{2a} \cdot e^{-\frac{9\pi^2 \tau\theta}{4a^2}} + \text{etc.}\right) \quad (168)$$

by which the temperature of the cube at any point is determined for any value of θ.

Remarks on the above solution. This example is one of the simplest that can be found on the solution of a partial differential equation when the state is not steady. It illustrates very well the great difference in character between ordinary and partial differential equations. The method here employed, of building up the complete solution as the sum of a series of particular solutions, each of which is a product of functions of a single variable, is very important. It corresponds to the conception of a musical note as the composite of a series of simply related notes known as "harmonics"; the resemblance is much more than a fanciful one, for vibrating mechanisms can be constructed which serve precisely as mechanical models for equations very similar to (153).

For the proof of the expansion (166) see Byerly's "Fourier's Series and Spherical Harmonics," Art. 26.

For further reading on partial differential equations which can be solved by similar methods see, — besides Byerly, — Woods and Bailey's "Analytic Geometry and Calculus," Chap. XVII; and Whittaker and Watson's "Modern Analysis," 3rd Ed., Chap. IX. The most recent view-point on such problems will be found in "Integral-Gleichungen," by A. Kneser.

19. The Problem of Intermittent Extraction. One of the most important types of processes in chemical engineering is the case where one reacting material flows at a uniform rate through another reacting material which is stationary with respect to the moving material. This is most commonly found in intermittent extraction, where a solvent is flowing through an extraction chamber containing a solid material part of which is soluble in the moving liquid. Examples of this may be found in the extraction of tannin from bark by means of water, the removal of color from sugar

syrup by means of bone char, and the removal of poisonous gases from air by gas mask cannisters.

Consider an extraction chamber of uniform cross-section through which liquid is flowing at the uniform rate of u pounds per hour. The liquid is removing an extractable material from the solid with which the chamber is filled. Let

y = concentration of the extractable material in the liquid,
z = concentration of the extractable material in the solid.
α = volume of liquid per foot length of tube.
β = volume of solid per foot length of tube.

Let the symbol d refer to increment of distance x along the tube, while Δ refers to time increments. Consider as usual a section of tube between the points x and $x + dx$.

Let

$\bar{y}$ = average value of y at the point x during time $\Delta\theta$.

Then

$\bar{y}u\Delta\theta$ = input of extractable material across the section at x during time $\Delta\theta$.

and

$\bar{y} + d\bar{y}$ = average value of y at point $x + dx$ during time $\Delta\theta$

hence

$(\bar{y} + d\bar{y})\, u\Delta\theta$ = output of extractable material across the section at $x + dx$ during time $\Delta\theta$.

By subtraction

$$\text{input minus output} = -\, u\, d\bar{y}\, \Delta\theta \qquad (169)$$

which must be equal to the increase in extractable material in the space between x and $x + dx$ during time $\Delta\theta$.

Next let y' = average value of y over the space interval dx at time θ. Then $\alpha y' dx$ = amount of extractable material contained in the liquid in this space at time θ.

Let z' = average value of z over interval dx at time θ. Then $\beta z' dx$ = amount of extractable material contained in the solid in this space at time θ. Hence

$(\alpha y' + \beta z')\, dx$ = total extractable material in this space at time θ. At the time $\theta + \Delta\theta$, the quantity y' has become $y' + \Delta y'$ and z' has become $z' + \Delta z'$. Therefore

$[\alpha (y' + \Delta y') + \beta (z' + \Delta z')]\, dx$ = total at time $\theta + \Delta\theta$. By subtraction

$$[\alpha \Delta y' + \beta \Delta z']\, dx = \text{increase during time } \Delta\theta \qquad (170)$$

and by equating values from (169) and (170)

$$u\, d\overline{y}\ \Delta\theta + \alpha\ \Delta y'\, dx + \beta\ \Delta z'\, dx = 0 \qquad (171)$$

We now divide by $dx\ \Delta\theta$ and let these increments approach zero. The average values approach as their limits the values at (x, θ). The result is

$$u \frac{\partial y}{\partial x} + \alpha \frac{\partial y}{\partial \theta} + \beta \frac{\partial z}{\partial \theta} = 0 \qquad (172)$$

This is the equation of continuity for the type of extraction process in question.

PROBLEMS

1. A current of air, containing 0.0004% CO_2, is passed through a long straight tube of uniform cross-section packed with small lumps of freshly prepared CaO. If after passing through 2 ft. of tube the CO_2 content has fallen to 0.0002%, what will it be after four feet?

2. With the apparatus of Prob. 1, assume the entering current to consist of 50% helium and 50% CO_2 by volume. Again suppose the per cent CO_2 to fall to half its value after 2 ft. What will it be after 4 ft.?

Hint. It may still be assumed that the CaO is in excess, but the volume changes due to absorption of CO_2 are too great to be neglected. Assume the rate of absorption of CO_2 at any point to be proportional to the concentration of CO_2 at that point. Set up equations of continuity both for CO_2 and for He.

3. Complete the calculation in Ex. (V).

4. In the drier of Ex. (V), suppose air enters substantially moisture free and leaves carrying 0.1 lb. water vapor in each lb. of air (on a dry basis). The stock is kept at a temperature such that the water in it is in equilibrium with air holding 0.2 lb. water vapor per lb. of air. The rate of evaporation at each point is proportional to the difference between this last figure and the moisture content of the air at that point, and also proportional to the water content of the stock. Find how long it takes the stock to pass through the drier, all other data being as in Ex. (V).

Hint. Set up the equation of continuity for the flow of moisture.

5. Repeat Prob. 4, assuming that air enters, not moisture free, but carrying 0.05 lbs. water vapor per lb. of air on a dry basis, all other data remaining the same.

6. With the notation of Ex. (W), prove that if the temperature is symmetrical about the axis of a cylinder, and does not vary in the direction of this axis,

$$\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} = \frac{s\rho}{k}\frac{\partial T}{\partial \theta}$$

where r is the distance from the axis.

7. With the notation of Ex. (W), prove that if the temperature is symmetrical about the origin,

$$\frac{\partial^2 T}{\partial r^2} + \frac{2}{r}\frac{\partial T}{\partial r} = \frac{s\rho}{k}\frac{\partial T}{\partial \theta}$$

where r is the distance from the origin.

8. With the notation of Ex. (W), prove that in general

$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} = \frac{s\rho}{k}\frac{\partial T}{\partial \theta}$$

where x, y, and z are rectangular coördinates.

9. With the apparatus and data of Prob. 2, set up the differential equations of the process, assuming that the CaO is no longer fresh enough so that the conditions may be taken as steady. Assume the rate of absorbtion of CO_2 at any point to be proportional to the product of the concentration of CO_2 and the strength of the lime at that point. Can you integrate these equations? In these assumptions, what fact has been neglected?

10. In the removal of color from sugar syrup by passing the syrup through bone charcoal, the color is adsorbed on the surface of the

char under such conditions that, at least during the early part of a run, we may assume the equation $\frac{\partial z}{\partial \theta} = ky$, with notation of equation (172). Furthermore the amount of liquid is so small in proportion to the amount of char that the term in α may be neglected. Integrate equation (172) under these conditions and state in words the meaning of your result.

11. With the apparatus and data of Prob. 1, set up the differential equations of the process, assuming, as in that problem, that volume changes are so slight as to be negligible, (because the concentration of CO_2 is small), but taking the CaO as no longer fresh. Assume the rate of absorption at any point to be proportional to the difference between the concentration of CO_2 in the air and the concentration of CO_2 on the lime. (This is essentially the same as the problem of a gas-mask.) Discuss the validity of these assumptions.

12. With the cube of Ex. (W), suppose a pair of opposite faces to be kept for a time at 0° and 100° respectively, the four remaining faces being perfectly insulated. When a steady state has resulted, the hot face is suddenly placed in contact with a cooler at 0°, both the opposite, conducting, faces being maintained at 0° thereafter. Find the temperature at each point of the cube as a function of the time, given the expansion

$$x = 2\left(\frac{\sin x}{1} - \frac{\sin 2x}{2} + \frac{\sin 3x}{3} - \cdots\right)$$

when $0 < x < \pi$.

13. Repeat Prob. 12, if the hot face is left at 100° and the cool face is suddenly raised to 100° and kept there.

14. Suppose the cube to be initially at 100° throughout. A pair of opposite faces are suddenly reduced to zero and kept there, the other faces being perfectly insulated. Find the temperature at any point as a function of the time.

15. Two iron slabs each 20 cm. thick, one of which is at the temperature 0° and the other at 100° throughout are placed together face to face, and their outer faces are then kept at the temperature 0°. Find the temperature of a point in their common face and of points 10 cm. from the common face fifteen minutes after the slabs have been put together. Given $\tau = 0.185$ in C. G. S. units, and that the series

$$\frac{2}{\pi}\left[\frac{\sin x}{1} + \frac{2\sin 2x}{2} + \frac{\sin 3x}{3} + \frac{\sin 5x}{5} + \frac{2\sin 6x}{6} + \cdots\right]$$

is equal to 1 from $x = 0$ to $x = \frac{\pi}{2}$ and is equal to zero from $x = \frac{\pi}{2}$ to $x = \pi$.

CHAPTER VI

THE GRAPHICAL EVALUATION OF INTEGRAL EXPRESSIONS

20. Reasons for Graphic Evaluation. Differential equations for physical or chemical processes are often of such a nature that integration by elementary algebraic methods is impossible. It may also happen that the relation between the variables is not known theoretically but only from an empirical curve derived from experimental data. It is possible to evaluate the integrals of such equations graphically. It is also frequently possible to save time by evaluating graphically integral expressions which can be solved by purely algebraic means but which are very time consuming when solved in that way.

Graphical evaluation depends upon the well known fact that the integral of the expression ydx is the area under the curve obtained by plotting y against x.

Example (*X*). In the simple distillation of a mixture of two volatile liquids, if the composition of the vapor leaving the liquid has been determined experimentally, it is possible to derive an equation from which can be calculated the composition of the distillate and of the residue after a given fraction of the original liquid has been distilled off.

Lord Rayleigh found the following relations between the composition of the liquid and of the vapor for mixtures of acetic acid and water, where " composition " means weight of acetic acid per unit weight of mixture.

Suppose that a mixture of acetic acid and water weighing W pounds at time θ and containing a pounds of acetic acid and $W - a$ pounds of water, be subjected to a simple dis-

tillation such that the vapor leaving the still is always in equilibrium with the liquid in the still. (Under these conditions, the composition of the vapor will have with the composition of the liquid the relations of Fig. 5.) The composition of the liquid at any time will be $\frac{a}{W}$ with respect to the acetic acid, and the composition of the vapor leaving the liquid at that time will be found from a curve as shown in Fig. 5, constructed from the following data, calling the composition of the liquid and the vapor x and y respectively.

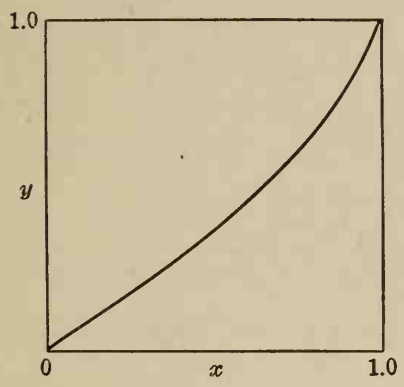


FIG. 5.

Composition of liquid x	Composition of vapor y
0.0677	0.0510
0.1458	0.1136
0.2682	0.2035
0.3746	0.2810
0.4998	0.3849
0.6156	0.4907
0.7227	0.6045
0.8166	0.7306
0.9070	0.8622

Allow dW parts of the liquid to evaporate. This portion of vapor will contain da parts of acetic acid. There will remain in the liquid $W - dW$ parts of a mixture containing $a - da$ parts of acetic acid, the composition of the distillate being $\frac{da}{dW}$.

Since $a = xW$ and y is the composition of the vapor,

$$y = \frac{da}{dW} = \frac{d(xW)}{dW} = \frac{xdW + Wdx}{dW} = x + \frac{Wdx}{dW} \qquad (173)$$

whence

$$\frac{dW}{W} = \frac{dx}{y - x} \qquad (174)$$

and by integrating between any two selected values of x, which we may call x_1 and x_2,

$$\ln \frac{W_2}{W_1} = \int_{x_1}^{x_2} \frac{dx}{y - x} \tag{175}$$

Even though we do not know the equation of the curve in Fig. 5 showing the relation between y and x, the evaluation

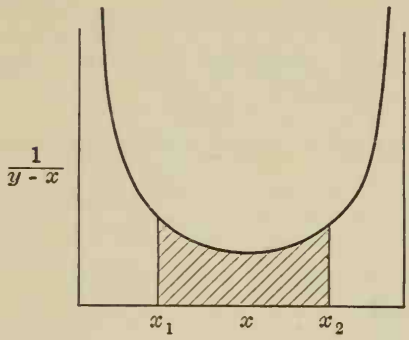


FIG. 6.

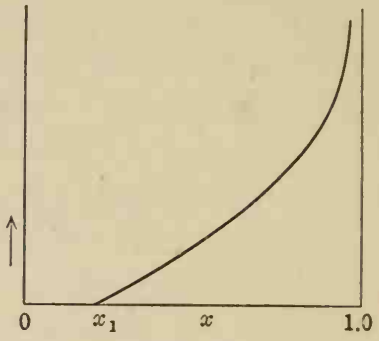


FIG. 7.

of the integral on the right side of the equation is practicable by the graphical method. Construct a curve with $\frac{1}{y - x}$ as ordinate and with x as abscissa, as in Fig. 6. Measure the area under it between the proper limits as shown and place it equal to $\ln \frac{W_2}{W_1}$.

The integral curve of the right hand side of the equation may be constructed in the same way, by keeping x_1 fixed and selecting successively greater values of x_2 and determining the area under the curve for each value of x_2 as above, giving a curve of the form shown in Fig. 7, where the ordinates are the values obtained for the right side of equation (175) as described, and are therefore equal to the values of $\ln \frac{W_2}{W_1}$ desired. It will be noted that the integral curve is asymptotic to $x = 1.0$ and that if we take a new value for x_1 we shall get a new curve of similar form.

Example (*Y*). In some cases the plot of y versus x must be made with two different scales for x in order to get the necessary precision.

Suppose that the data be plotted as shown in Fig. 8, it being necessary to measure the area under the curve between the limits of $x = 1$ and $x = 100$. In order to get the necessary precision in y between the limits of $x = 1$ and $x = 1.5$, it is necessary to use the x scale of the size shown

FIG. 8.

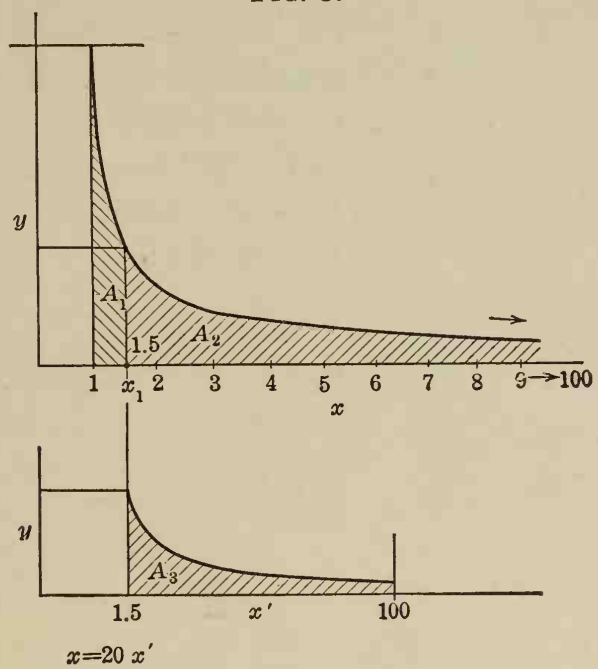


FIG. 9.

in Fig. 8. But when this size is used the paper is not long enough to include $x = 100$. Therefore make a new plot of the data from $x = 1.5$ to $x = 100$ with the same ordinates as in Fig. 8 but with the abscissae 1/20 of the ones before, giving the curve shown in Fig. 9.

The area under the curve in Fig. 8 between the limits of $x = 1$ and $x = 1.5$ may now be measured and found to be equal to A_1. The area under the curve in Fig. 9 between the limits of $x = 1.5$ and $x = 100$ may now be measured and

found to be equal to A_2. Since the abscissae in the second figure are 1/20 of those in the first and since the ordinates are the same, one square inch in the second figure will equal 20 square inches in the first. Therefore basing the evaluation on the first figure, the evaluation of the expression desired will be

$$A_1 + 20\,A_3 = \int_{x=1}^{x=100} y\,dx$$

Fig. 10.

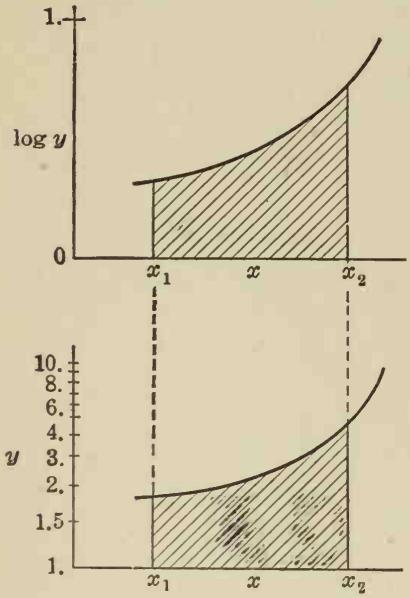


Fig. 11.

Example (*Z*). The evaluation of definite integrals by the graphical method when the units of the graph are more complicated requires considerable care. For instance, suppose that it was desired to evaluate the integral $\int_{x_1}^{x_2} \log y\,dx$. This may be done by plotting $\log y$ versus x and measuring the area under the curve as before. On the other hand, the same curve is obtained by plotting y versus x on semi logarithmic paper. These curves are shown in Figs. 10 and 11. The areas will be identical only when the distance between $\log y = 0$ and $\log y = 1$ on the ordinates of Fig. 10 is the same as the distance between 1 and 10 on the ordinates of the semilogarithmic paper, Fig. 11.

Example (*AA*). The problem involved in determining the area under a curve between limits of x when the curve becomes infinite with respect to y, is one frequently met especially in connection with thermodynamic equations in physical chemistry.

For instance it may be shown that the minimum work

required to completely vaporize a volatile substance from a solution containing n mols of that substance at the partial pressure p is equal to

$$RT \int_n^0 \ln \frac{P}{p} dn$$

where P is the vapor pressure of the pure substance at the temperature T, a constant, and R is the gas constant.

This integral may be evaluated graphically by plotting $\ln \frac{P}{p}$ as ordinate and n as abscissa, measuring the area under the curve between the limits of $n = n$ and $n = 0$. The curve has the shape shown in Fig. 12. It will be noted, however, that p approaches zero as n approaches zero, whence the value of $\ln \frac{P}{p}$ becomes infinite. The problem resolves itself into the determination of the area under the curve where the curve recedes to infinity at the point $n = 0$.

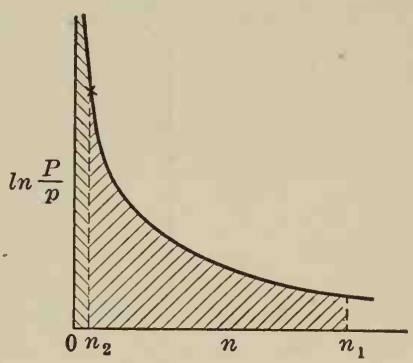


FIG. 12.

There are several ways of doing this. One way is to measure the area under the curve between the points n_1 and n_2 by any suitable means such as by Simpson's rule or by means of a planimeter, selecting the point n_2 such that the laws of dilute solution apply approximately between n_2 and 0. The remaining area from n_2 to 0 may be estimated as follows, the area thus obtained being added to the other area to give the total value required, —

Assume that between the limits of n_2 and 0 the value of p is a linear function of n in agreement with Henry's law, or $p = an$. Substituting this in the original equation gives

$$RT \int_{n_2}^0 \ln \frac{P}{an} dn \qquad (176)$$

which gives by direct integration

$$n_2RT\left(\ln \frac{P}{an_2} + n_2\right) \tag{177}$$

which is finite.

Example (*BB*). Rittinger's law states that the energy needed for crushing a given weight of material is proportional to the surface developed.

In commercial practice when a material is crushed, the resulting particles are of varying size, the percentage of each size being determined by means of a screen analysis. The result of such an analysis is shown in Fig. 13.

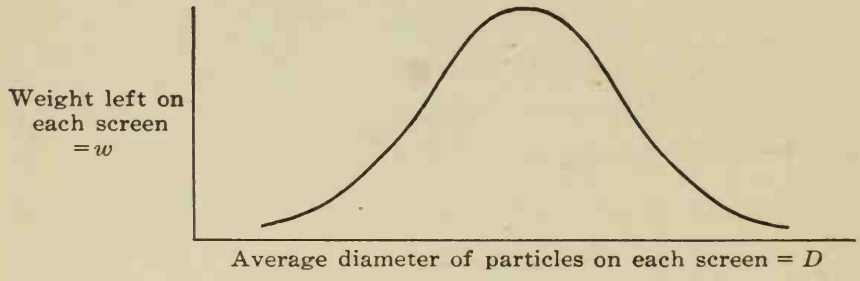


FIG. 13.

The amount of energy needed to crush a ton of coal from one screen analysis to another may be estimated from Rittinger's law in the following manner.

Let w be the weight of coal on any one screen after such an analysis, where D is the average diameter of the particles on that screen, and let there be n particles of that size. Therefore

$$w = anD^3 \tag{178}$$

where a is a proportionality constant. In the same way the surface of the coal particles on that screen will be

$$s = bnD^2. \tag{179}$$

Since a and b are constants, the relation of the surface of the particles to the volume will be

$$s = kx/D \tag{180}$$

where x is the volume of the particles on the screen, and k is another proportionality constant.

Assume now that the number of screens is large so that only a small number of particles are caught on any one screen. The last equation may then be written in differential form

$$ds = \frac{k\,dx}{D}. \tag{181}$$

The total surface of all the particles on all the screens will then be the summation of the surfaces of those on each of the individual screens, or

$$S = \int ds = \int \frac{k\,dx}{D}. \tag{182}$$

The right hand side of this equation may be evaluated graphically, if it is remembered that the volume of the coal

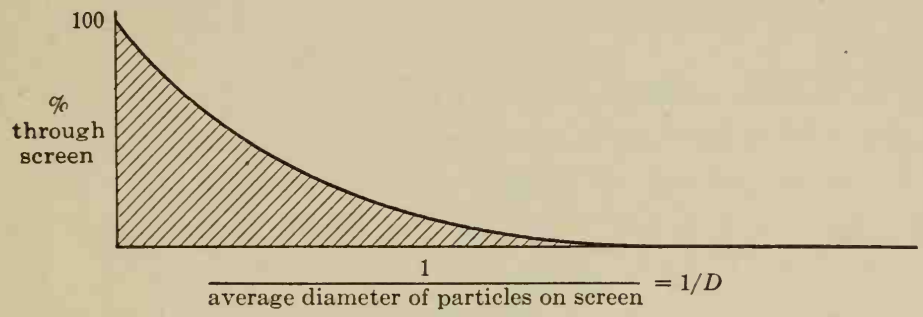


FIG. 14.

is proportional to its weight, by taking as a basis 100 parts of original coal, and plotting as ordinates the percentage which has passed through a given screen diameter D against the reciprocal of D as abscissae, as shown in Fig. 14.

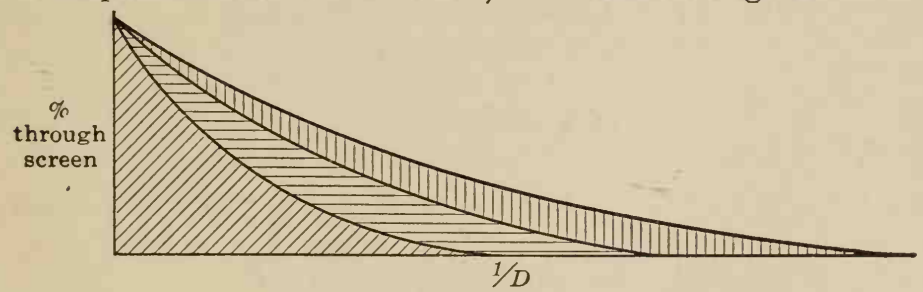


FIG. 15.

The area of the space under the curve so obtained is therefore proportional to S. If the areas be obtained for three screen analyses before and after crushing twice, the ratio of

the first two areas will be to the ratio of the second and third areas, as the power consumption in the first crushing is to that in the second crushing. Such a plot is shown in Fig. 15.

Example (*CC*). The vapor pressure of a volatile liquid as a function of the temperature is expressed by the Clapeyron equation

$$\frac{dp}{dT} = \frac{L}{(V - v)\,T} \tag{183}$$

which may be simplified by assuming the Perfect Gas law to hold and by neglecting the volume of the liquid as compared with the volume of the vapor, giving the approximate form

$$\frac{d \ln p}{dT} = \frac{L}{RT^2} \tag{184}$$

where L is the latent heat of vaporization of one mol of the liquid and R is the gas constant.

It is customary to integrate this equation by assuming that L is substantially a constant, which is true over short temperature ranges. But over longer ones this is not true, and great errors may be introduced by such an assumption. For instance, the value of L for methyl alcohol varies from 9.2 at 0° C., to 1.4 at 238.5° C. It is possible to obtain a much more precise value for the vapor pressure by allowing L to remain a variable and evaluating the integral expression graphically.

The equation may be written

$$\int_{p_1}^{p_2} d \ln p = \int_{T_1}^{T_2} \frac{L}{RT^2} dT \tag{185}$$

To evaluate the right side, plot $\frac{L}{RT^2}$ against T, where T is the temperature in absolute degrees, R is 1.99 when L is expressed in heat units, and the value of L is known empirically. The area under the curve between the proper values of T is the evaluation of the integral expression desired.

PROBLEMS

1. Using the data of Ex. (X) plot on graph paper two integral curves as illustrated by Fig. 7, using for one of them $x_1 = 0.15$ and for the other $x_1 = 0.70$.

2. Evaluate $\int_0^{10} \frac{e^{-0.05x}\,dx}{x + 0.01}$. To how many significant figures is your answer correct?

Suggestion: Here is a simple case where the "indefinite integral" cannot be expressed in finite terms by means of the elementary functions. A graphic process similar to Ex. (Y) is easy to use. It is also easy to expand the integrand in a series. These two methods may well be used to check each other.

3. Find the value of $\int_0^1 \ln (1 + x)\,dx$.

(*a*) by plotting $\ln (1 + x)$ on ordinary graph paper,
(*b*) by plotting $1 + x$ on semi-log paper,
(*c*) by the usual method of finding the indefinite integral.

To how many significant figures do your answers check?

4. Derive (177) from (176). What is the physical meaning of the constant a? What data are needed in order to determine the numerical value of a?

5. A certain material was passed through a tube mill at a fixed rate, the power consumption being found to be 1.4 K.W. hours per ton of material ground. The mill was then doubled in length and similar material was fed at the same rate as before. Estimate the power consumption required theoretically in the second case from the following screen analyses. (See next page.)

6. Discuss the logic of Ex. (*BB*) by which, in obtaining equation (181), a finite quantity s was changed into a differential ds. What other steps of similar character must be taken in obtaining (181)?

7. In Ex. (BB) what would be the value of the ratio b/a if all the particles were perfect spheres? What if they were all perfect cubes? What if they were all small flat cylinders with diameters ten time their thickness? What are we assuming when we take a and b to be constants?

8. The latent heat of vaporization of methyl alcohol was determined by experiment as follows:

$t°$ C.	0	50	60	70	100	200	230
cal/gm. mol	9263	8781	8630	8473	7880	4863	2706

From these data plot a smooth curve of L against t. By the method of

Ex. (CC) draw a curve from which the rise in the vapor pressure of methyl alcohol with temperature can be read off.

Data for Problem 5

Mesh	Opening in inches	Feed % left on screen	First product % left on screen	Second product % left on screen
2	.4	0		
3	.263	6	0	
4	.185	10	2	
6	.131	18	6	
8	.093	18	11	0
10	.065	16	17	7
14	.046	12	14	9
20	.0328	9	14	12
28	.0232	8	14	20
35	.0164	3	8	13
48	.0116		8	13
65	.0082		4	9
100	.0058		2	6
150	.0041			5
200	.0029			4
Through 200				2

MISCELLANEOUS PROBLEMS

The following problems depend upon the principles and methods of reasoning illustrated in the foregoing chapters, rather than upon the precise formulas which have been obtained in special examples.

1. In a tank are 100 gals. of brine containing 50 lbs. of dissolved salt. Water runs into the tank at the rate of 3 gals. per min., and the mixture runs out at the rate of 2 gals. per min., the concentration being kept uniform by stirring. How much salt is in the tank at the end of one hour?

2. In Prob. 1, suppose the outflow passes through a second 100 gal. tank initially filled with pure water. How much salt will this tank contain at the end of 1 hour?

3. Suppose that bacteria grow at a rate proportional to the number present, but that they produce toxins which destroy them at a rate proportional to the number of bacteria and to the amount of toxin. Suppose further that the rate of production of toxin is proportional to the number of living bacteria. Show that the number of bacteria increases to a maximum and then falls off toward zero, but that under these conditions the colony will never become extinct.

4. Two vertical cylindrical tanks each 10 ft. deep and 4 ft. in diameter are connected by a short 2-inch pipe at the bottom. If one of the tanks is full and the other empty, find the time required to reach the same level in both. Assume that the velocity through the pipe is the same as that through an orifice under the same effective pressure.

5. Assuming that the density of sea water under a pressure of p lbs. per sq. in. is

$$1 + 0.000003\,p$$

times its density at the surface, show that the surface of an ocean 5 miles deep is about 450 ft. lower than it would be if water were incompressible.

6. If half the water runs out of a conical funnel in 2 min., find the time required to empty. Assume the rate of flow to be proportional to the square root of the pressure.

7. A brick wall is 30 cm. thick. If the inner surface is at 20° C., and the outer at 0° C., compute the heat loss per day through 100 sq. m. of this wall. Take the conductivity as 0.0020 in C. G. S. units.

How much coal must be burned to compensate this loss if the heat of combustion is 7000 cal/gram and the efficiency of the furnace 60%?

8. Two steam pipes 20 cm. in diameter protected with 10 cm. thick covering of concrete (conductivity 0.0022) and magnesia (conductivity 0.00077) are run underneath the soil. If the outer surfaces are at 30° C. and the pipes themselves are at 160° C., compute the heat losses per sec. per cm. length in the two cases.

9. A hollow lead sphere (conductivity 0.0827) whose inner and outer diameters are 1 cm. and 10 cm. respectively is heated electrically by a 10 ohm coil placed within the cavity. What current will keep the surfaces at a steady difference of 5° C.?

10. A wire whose resistance per centimeter length is 0.1 ohm is embedded along the axis of a cylindrical cement tube of radii 0.5 cm. and 1.0 cm. An electric current of 5 amp. is found to keep a steady difference of 125° C. between the inner and outer surfaces. What is the conductivity of the cement?

† **11.** A radioactive substance R_1 decays forming R_2, the period being 3 weeks. R_2 in turn decays to R_3, the period being three days. (The period of a radioactive change is the time needed for the amount of decaying substance, if initially pure, to fall to half its initial value.) Plot a curve showing the rate at which R_3 builds up if R_1 is initially pure. Plot also a curve showing the life of R_2.

12. The natural growth of population would cause the total number of inhabitants of the country to double in k years if there were no immigration, which, however, brings a constant influx at the rate of b persons per year. Assuming the natural increase among the immigrant population to be the same as among the native element, in how many years will the population double?

† **13.** Repeat Prob. 12, assuming the natural increase among the immigrant population to be m times as rapid as among the native element.

† **14.** With the notation and assumptions of Prob. 13, what is the maximum value of b if the foreign population is never to exceed the native?

15. Repeat Prob. 14 assuming that any person is to be counted as a native whose ancestors immigrated p or more years before his birth.

16. In drying a sheet of heel board, water was lost thus:

When θ	=	0	66	175	251	352	449	491	573
water	=	503.3	384.4	202.8	102.7	50.2	29.6	24.3	16.7
θ	=	616	750	minutes					
water	=	15.4	15.2						

What was the probable order of the process?

17. Hydrogen dioxide H_2O_2 was observed to decompose in water thus:

When θ	=	0	10	20	hours
H_2O_2	=	22.8	13.8	8.25	units

where the unit of H_2O_2 is taken as the number of c.c. $KMnO_4$ solution needed to titrate a definite volume of solution. Find the velocity constant on the assumption that the reaction is of the first order.

18. With the data of Prob. 17, find the probable amount of H_2O_2 remaining after 40 hours.

19. In a first order process the following observations were made on the product x of the reaction:

When θ	=	0	10	20	30	40	50	60	∞
x	=	0	60.8	97.7	119.9	133.4	144.4	146.1	153.8

Determine the value of the velocity constant by the method of averages.

20. It is empirically true that if the daily production of an oil well is plotted on log-log paper against the time since the well started to flow, the result will be a straight line. Show that the total production up to time θ is given by the formula $P = \frac{a}{n}\theta^n$ where a and n are constants. Show how these constants may be determined from the daily production plot.

21. It does not pay to operate an oil well after the daily flow has dropped to an amount b. With the notation of Prob. 20, show that the total yield up to that time is $\frac{a}{n}\left(\frac{b}{a}\right)^{\frac{n}{n-1}}$. Find also the time when this yield is attained.

22. A substance x is formed in agreement with a differential equation of the form

$$\frac{dx}{d\theta} = k\,(a - x)^n$$

Show how the process may be represented by a straight line on log-log paper.

23. Suppose the amount of the yield x in Prob. 22 to be known by means of an empirical curve for all values of θ. (This curve is on ordinary plotting paper.) Show how to determine the constants k, a, and n.

24. A substance x is formed in agreement with a differential equation of the form

$$\frac{dx}{d\theta} = k\,(a - x)\,(b - x)$$

and the yield x is known for all values of θ. Show how to determine the constants k, a, and b.

25. Rubber is vulcanized by mixing it with sulphur and other reagents and subjecting the mixture to heat for a period of time. The combination of the sulphur with the rubber takes place at a rate which, for short periods, is proportional to the amount of free sulphur present and also to the difference between the amount of sulphur present as combined sulphur and the amount of combined sulphur which would be present if all the rubber had combined with sulphur. (100 parts of rubber combine with 47 parts of sulphur.) For longer periods it is found that the rate of combination is further proportional to a function of the time θ determined empirically to be of the form $a\theta^{n+1} + \theta$, where a and n are constants. Test the following runs with reference to their agreement with the above statements:

Run (*a*)

When θ =	6	8	10	12	14	16	18	20	22	24	min.
S =	3.70	3.18	3.22	3.17	3.03	2.91	2.84	2.82	2.68	2.53	

where S = parts free sulphur per 100 parts rubber.

Run (*b*)

When θ =	8	12	16	20	24	28	min.
S =	1.26	1.00	0.80	0.70	0.50	0.37	

Also estimate the free sulphur at the start.

26. The rate of solution of a salt in water is proportional to the difference in concentration between the saturated film of solution on the surface of the crystal and the concentration in the solution. (Where the amount of crystals is large, the decrease in their surface may be neglected during the first part of the dissolving process.) The proportionality constant depends on the efficiency of the agitator. With a simple paddle wheel stirrer the following run was made:

Volume of solution = 4000 cc. Weight of crystals $K_2Cr_2O_7$ = 1000 gms. Temperature = 23° C.

θ =	0	5	10 minutes
c =	0	1.60	1.93 equivalents per litre.

A second run under similar initial conditions with propeller and draft tube:

θ =	0	7.5
c =	0	1.95

Find the ratio of the proportionality constants in the two cases.

27. A crystal of $K_2Cr_2O_7$ falls through a column of pure water. After falling 10 ft. it is $\frac{1}{2}$ dissolved. How far must it fall to completely disappear? Assume the diffusion coefficient proportional to the velocity of the crystal through the liquid, and the stream lines of liquid about the crystal smooth.

28. A mass of crystals of potassium bichromate of substantially uniform size is suspended in water by continued, constant agitation. The amount of water used is many times that required to give a saturated solution. At the end of 10 mins. of agitation, titration of the solution shows that half of the $K_2Cr_2O_7$ has dissolved. How much longer must the agitation be kept up to dissolve it all?

29. One gram mol each of potassium persulphate and phosphorous acid were mixed, in excess of water, with 0.0569 gm. mol. hydriodic acid. A first reaction was

$$K_2S_2O_3 + 2\,HI = K_2SO_4 + H_2SO_4 + I_2$$

which was accompanied by the consecutive reaction

$$H_3PO_3 + I_2 + H_2O = H_3PO_4 + 2\,HI$$

Both reactions are known to be of the second order. The constants were found to be $k_1 = 0.0033$ and $k_2 = 0.079$ respectively. Plot curves showing the amounts of iodine and of persulphate at time t (hours).

30. Potassium permanganate and oxalic acid, in the proportion of two molecules of the former to five of the latter, were mixed with excess of sulphuric acid, manganese sulphate, and water. A first reaction was:

$$2\,KMnO_4 + 3\,MnSO_4 + 2\,H_2O = 5\,MnO_2 + K_2SO_4 + 2\,H_2SO_4$$

accompanied by the consecutive reaction

$$MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2\,H_2O + 2\,CO_2$$

The amount of oxalic acid was observed to change thus:

When t =	2	3	4	5	6	7	8	9	min.
$H_2C_2O_4$ =	51.9	42.4	35.4	29.8	25.7	22.2	19.4	17.3	

Determine the constants k_1 and k_2 of the reactions, and then make a table showing the agreement of calculated with observed values for the oxalic acid.

31. The corrosion of iron under water is known to be a function of the temperature, of the velocity of the water by the surface of the metal,

and proportional to the oxygen concentration in the water. Formulate differential equations for the rate of corrosion at constant temperature.

(*a*) in a closed vessel such that no oxygen is present other than that dissolved in the water at the start;

(*b*) in an open vessel permitting the diffusion of oxygen into the water at a rate proportional to the difference between the oxygen concentration in the air and that in the water;

(*c*) in a pipe through which water flows at a constant rate.

32. The equilibrium concentration of tannin on tanbark may be represented by the adsorption equation

$$c = kx^{\frac{1}{m}}$$

The tanbark is to be extracted with water flowing by the bark, the rate of extraction being proportional to the difference between the concentration of the tannin in the solution in contact with the bark and the equilibrium concentration in the surface film of solution on the bark itself given by the above formula. Set up differential equations for the rate of extraction

(*a*) in a continuous counter-current system;

(*b*) in an intermittent system where the bark is stationary and the liquid flows at a constant rate.

33. Show that in a counter-current air-drier we have

$$dW = kW\,(M - W)\,dx$$

where W is the total water content of the stock passing a section at a distance x from the end where the stock enters per unit time. What can be said of the quantities k and M?

34. It is known that within the temperature range from 200° C. to 500° C. the rate at which a hydrocarbon oil, such as petroleum, cracks or decomposes into lighter hydrocarbons and carbon doubles approximately for every 10° C. rise in temperature. A 1000 barrel still is charged with oil, brought up to 350° C., and distilled off in the presence of injected steam at a uniform rate over a period of sixty hours. The cracking is estimated at 40%. How much more rapidly would it be necessary to distill it at 400° C. to keep the cracking the same?

35. With the data of Prob. 34, the oil can if desired be distilled at a progressively increasing temperature. If the distillation is started at 300° C. and finished at 400° C.. the distillation rate being constant and the rate of increase of temperature being also constant, what time must

be taken for the distillation in order to keep the cracking the same as before?

36. In commercial practice, crude petroleum is refined in a series of 10 continuously operated stills, each holding 1000 barrels. The feed, 10,000 barrels per day, enters one end of the first still, flows through it and leaves at the opposite end, whence it enters the beginning of the second still, and so on through the series. From each still 900 barrels per day is distilled off, and the final residue of 1000 barrels is discharged from the last still. The temperature at which the distillation starts in the first still is 300° C., in the second 10° C. higher, and so on. A uniform temperature gradient may be assumed through each still. Using the data of Prob. 34 so far as necessary, make a table or a graph showing (*a*) the amount of cracking realized in the stock leaving each successive still and (*b*) the time the stock leaving each still has been under distillation.

37. CO is produced by passing pure CO_2 at atmospheric pressure up through a bed of coke kept by electrical heating at a substantially constant temperature sufficiently high so that at equilibrium the reduction is practically complete. A two foot depth of fuel gives a gas 60% CO. (*a*) How deep must the bed be to give 95%? (*b*) How much more slowly must the gas enter to give 95% with the same depth of fuel? Discuss the validity of the assumptions made in your solution.

38. The ammonia is to be removed from a dilute aqueous solution at 20°, containing one per cent ammonia, by aeration. If 99% of the ammonia is removed in this way how many cu. ft. of air must be employed per pound of ammonia removed? Given that the vapor pressure of water at 20° = 17.4 mm. Hg. and v.p. of NH_3 above a 1% solution at 20° = 16 mm. Hg. Assume that v.p. of NH_3 is proportional to the concentration of the solution.

39. Repeat Prob. 38, supposing the original solution to be 5%.

40. Sugar is fermented in open vats to alcohol at 25° C., the original sugar solution being of such strength as to produce a 10% product. At the temperature of the process the product exerts a pressure of 32 mm. of which 11.83 is alcohol and 20.17 is water, the composition of vapor over a 10% alcohol solution being 60% alcohol by weight. One mol of CO_2 is formed for every mol of alcohol. Neglecting any water loss, estimate the percentage of the total alcohol formed which is lost during fermentation.

(*a*) assuming that the partial pressures are not lowered by the sugar;

(*b*) assuming the partial pressure of the alcohol and of the water depressed by the presence of the sugar in accordance with Raoult's law.

41. A dust particle settles in air at a substantially constant rate. The rate is a function of the size of the particle, the smallest falling at the lowest rate. One of the commercial processes for the removal of dust from air is by means of a settling chamber consisting of two horizontal parallel plates between which the air carrying dust flows horizontally at a rate slow enough to enable the particles to fall to the bottom. The velocity of the air along the walls is zero and increases toward the middle of the flue according to the formula from hydrodynamics

$$a^2 - y^2 = b^2x$$

where a is half the distance between the plates, y is the distance of an air particle from the middle of the flue, and x is the velocity of the particle, while b is a constant. Letting u denote the constant vertical velocity of the smallest dust particle, determine the length of flue needed to rid the air completely of dust, the constants a, b, and u being known.

42. With the tanks of Prob. 4, suppose that water flows in at the top of each tank at the constant rate of 4 cubic feet per minute, and furthermore that the second tank has an orifice in the bottom two inches in diameter. The first tank being initially full and the second empty as in Prob. 4, set up differential equations satisfied by the respective depths h_1 and h_2 at time θ. Study the changes in water level in the tanks.

43. A hot fluid is carried in a horizontal direction through a rectangular chamber by a very large number of very small pipes evenly spaced and near together. A cold fluid passes in a vertical direction through the space within the chamber outside the pipes. Set up differential equations satisfied by the temperatures of the two fluids on their way through the chamber, assuming a steady state. (Processes in which two different gases or liquids flow at right angles are of great practical importance.)

44. A coke oven consists essentially of two parallel walls of large extent, 18 inches apart, maintained at the constant temperature of 2600° F. The stock when first placed in the oven undergoes rapid changes of a complex character, but at a time which we may call $\theta = 0$ it may be assumed that the temperature of the stock is substantially uniform at 300° F. Thereafter it obeys the usual laws of heat flow. Plot a series of curves showing the temperature gradient through the stock at intervals of one hour. Given that the effective conductivity is 0.1 in B.t.u., the unit of length being one foot and the unit of time one hour. The density is 100 lbs./cu. ft. and the specific heat is about 0.5.

45. The specific heat of graphite is as follows:

$T°$ C.	−244	−186	−50.3	+10.8	+138.5
Sp. heat	0.005	.027	0.1138	0.1604	0.2542
$T°$ C.	+249.3	+641.9	+977.0		
Sp. heat	0.3250	0.4450	0.4670		

By graphic integration plot a curve showing the total heat content of graphite as a function of temperature.

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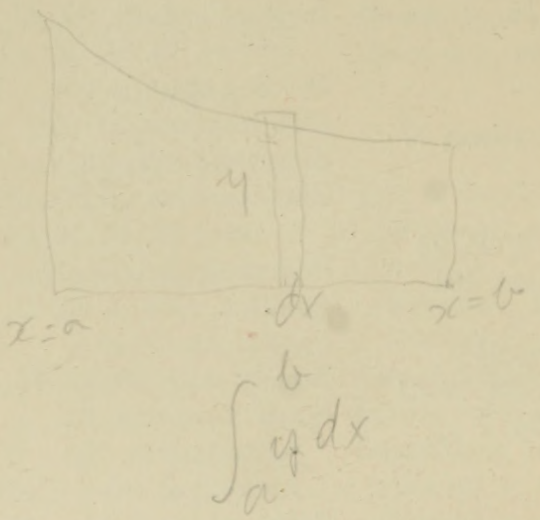
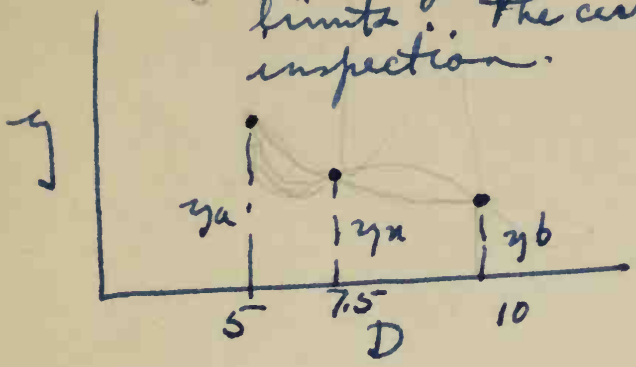


Preimodal formula to integrate Equation 64

$$y = \int_5^{10} \frac{1}{\sqrt{D-4} + 4\sqrt{D-2}}\, dD$$

Plot y against D between the limits. The curve is smoth by inspection.



y_a is y value when $D = 5$ $= \frac{1}{\sqrt{5-4} + 4\sqrt{5-2}}$

y_b is y value when $D = 10$

y_n is y value when $D = 7.5$

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a}$$

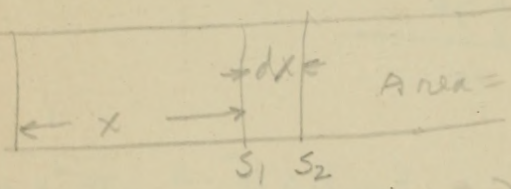
One dimensional Heat flow (Not steady state)

Q = rate of heat transfer across area A

k = conductivity of material = a constant.

$\frac{\partial t}{\partial x}$ = temperature gradient across A

$$Q = -kA\frac{\partial t}{\partial x}$$ (Newtons law.



at S_1 $Q_1 = -kA\frac{\partial t}{\partial x}$

at S_2 $Q_2 = -kA\left[\frac{\partial t}{\partial x} + d\left(\frac{\partial t}{\partial x}\right)\right]$

where d is a change in whatever stands after it
due to space change in x

$Q_2 - Q_1$ = rate at which heat is changing in the space $= kA\,d\left(\frac{\partial t}{\partial x}\right)$

Heat capacity = mass × sp. heat = vol × density × sp. heat

Heat capacity × rate of change of temperature

$$= (A\,dx\,\rho\,s)\left(\frac{\partial T'}{\partial \theta}\right)$$

$$kA\,d\left(\frac{\partial T}{\partial x}\right) = A\,dx\,\rho\,s\left(\frac{\partial T'}{\partial \theta}\right)$$

$$k\,\frac{d\left(\frac{\partial t}{\partial x}\right)}{dx} = \frac{kA\left(\frac{\partial t}{\partial x}\right)}{A\,\Delta x} = \rho s\frac{\partial T'}{\partial \theta}$$

as Δx becomes smaller

$$k \frac{\partial \left(\frac{\partial t}{\partial x}\right)}{\partial x} = \rho s \frac{\partial t}{\partial \theta}$$

$$k \frac{\partial^2 T}{\partial x^2} = \rho s \frac{\partial t}{\partial \theta}$$

Call $\frac{k}{\rho s} = \tau$ (Greek letter Tau)

To integrate

Get a formal solution that is get a function of x and θ which, substituted for T makes both sides identically equal.

Let $T = (y)(z)$ where y is a function of x alone and z is a function of θ alone. (This can not always be done.

When T is changing with respect to x z is a constant when T changes with respect to θ, y is a constant.

Hence substituting

$$\tau z \frac{\partial^2 y}{\partial x^2} = y \frac{\partial z}{\partial \theta}$$

$$\frac{1}{y} \frac{\partial^2 y}{\partial x^2} = \frac{1}{\tau z} \frac{\partial z}{\partial \theta}$$

Since no time terms are on the left the partials symbol is no longer necessary

$$\frac{1}{y} \frac{d^2 y}{dx^2} = \frac{1}{-\tau z} \frac{dz}{d\theta} = -C^2$$

A

$$\frac{d^2y}{dx^2} = -\gamma c^2$$

B

$$\frac{1}{T_3}\frac{dz}{d\theta} = -c^2$$

$$-T\omega^2\theta$$

when

for

$$\frac{d}{dx}$$

$$\frac{d^2}{dx^2}$$

$$T = A$$

$$\times e^{-T}$$

II Part.

Dete

condition

(a) wh

T

(b) wh

le

endar

et)

ed)

cx

$$\cos\frac{n\pi}{2a}x = dt = 0$$

Part III Initial conditions satisfied by a proper choice of the A terms.

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